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PENNSYLVANIA SALT MANUFACTURING COMPANY

FINAL RESEARCH REPORT

(Cumulative - January, 1953 through January, 1954)

PROJECT NR 352-304/2-1-52

CONTRACT NONR-807(00)

SODIUM PERCHLORATE: Research Leading Toward the Development of Selected Methods to Produce Sodium Perchlorate Without the Use of Platinum

SECTION A: The Development and Use of Lead Dioxide Anodes, Silicon-Silicon Carbide Anodes, and Miscellaneous Anode Materials

by

H. C. Miller
J. C. Grigger
F. D. Loomis

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SUBJECT

Sodium Perchlorate: Research Leading Toward the Development of Selected Methods to Produce Sodium Perchlorate Without the Use of Platinum (Project Number NR 352-304/2-1-52; Contract Number NONR-807(00).

OBJECT

To investigate methods for production of sodium perchlorate without the use of platinum; to include, but not necessarily be limited to, the following:

(1) The use of lead dioxide anodes.

(2) The use of anodes comprising silicon-silicon carbide.

(3) The disproportionation of sodium chlorate in acid solution.

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SCOPE

This final research report, titled Section A, covers work authorized by the Office of Naval Research for the development and use of lead dioxide, silicon-silicon carbide and miscellaneous anode materials as substitutes for platinum in the production of sodium perchlorate. Some initial work, done under Project NR 352-263/2-19-51, was carried out in the period from February through August, 1951; this included a literature review and preliminary laboratory work. Extended laboratory work was carried out continuously under the present Project NR 352-304/2-1-52 during the period of February 1952 through January, 1954.

A companion research, also part of the subject project, on the disproportionation of sodium chlorate in acid solution, has been covered in a separate final report, labelled Section B, which was issued December, 1953.

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SUMMARY

I. Lead Dioxide Anodes

A. Fabrication

1. Plating Baths

Massive lead dioxide electrodes were electroformed in both sheet and rod forms from a lead nitrate plating bath. The effects of temperature, current density, pH and additives on the deposition of massive lead dioxide from a lead nitrate bath were studied to determine conditions necessary to produce a hard, dense massive lead dioxide with a smooth, regular surface. Other baths for plating massive lead dioxide, including alkaline lead tartrate and acid lead perchlorate, were explored.

2. Base Materials

In the lead nitrate plating bath, tantalum and nickel were the only metals tested on which good quality massive lead dioxide could be plated. The quality of lead dioxide plated on spectrographic grade graphite rod was similar to that formed on a tantalum base. A continuous lead dioxide deposit could not be formed on other grades of graphite and carbon. Synthetic magnetite, silicon and Durhy materials showed some promise as base materials; however, their irregular surfaces prevented the formation of smooth, continuous massive lead dioxide deposits.

3. Safety in Plating

When handling lead compounds in formulating and operating lead dioxide plating baths, good housekeeping, rubber gloves, dust masks and sound sanitary habits are required to avoid lead intoxication.

B. Testing

1. Anode Performance

Massive lead dioxide anodes were tested in the chlorate-perchlorate cell without failure or deterioration at 3 to 25 amperes, and at current densities of 0.1 to 0.45 amp./cm.^{2}, for periods corresponding to nearly 60 days of continuous operation. A 100 ampere cell with a massive lead dioxide anode (3-1/2" x 14-1/2" x 5/8") was operated for 24 batch electrolyses of sodium chlorate for a total running time of 35.8 days at a current density of 0.28 amp./cm.^{2}, and a cell temperature of 30 to 50°C.

2. Base Material Performance

Tantalum, when used as a base for lead dioxide anodes, was not eroded in the chlorate-perchlorate cell. Other metals used as bases, such as nickel, Monel, copper and iron, were rapidly eroded. Durhy #2 and spectrographic grade graphite rods, when used as bases for lead dioxide anodes, were not eroded in brief tests carried out in the chlorate-perchlorate cell. Anodized lead tubing was rapidly eroded

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in the chlorate-perchlorate cell.

3. Anode Weight Loss

Weight losses of lead dioxide anodes in chlorate-perchlorate cell service do not appear to be much greater than those of platinum anodes, but are not comparable because the greater thickness and low material cost of lead dioxide anodes make these losses without significance.

4. Current Efficiencies

Lead dioxide anodes operated at an average current efficiency of 68% at current densities of 0.2-0.3 amp./cm.^{2} in the sodium chlorate concentration range of 600 to 100 g./l. At 0.1 amp./cm.^{2}, the average current efficiency was 53%. At 0.45 amp./cm.^{2} a higher current efficiency (78%) was found at 48°C. than at 15°C. (54%). In comparison, a 10 ampere platinum anode cell operated at a current efficiency of 89% at a current density of 0.3 amp./cm.^{2} and a cell temperature of 45°C. in the sodium chlorate concentration range of 600 to 100 g./l.

5. Sodium Chlorate Electrolyte Studies

The sodium chlorate electrolyte was prepared to a concentration of about 600 g./l., using a reagent grade salt. Current efficiency values were not appreciably changed by variations in electrolyte pH in the range of about 3 to 10, or temperature in the range of about 5° to 50°C.

Addition of sodium fluoride to the sodium chlorate electrolyte increased the current efficiency. However, on successive electrolyses with the same lead dioxide anode and sodium fluoride addition, the current efficiency dropped to below its original control value. The addition of sodium dichromate dihydrate at concentrations of 0.5 to 5 g./l. to the sodium chlorate electrolyte lowered the cell current efficiency to 27% and 16% respectively.

After electrolysis with a lead dioxide anode, the chlorate-perchlorate electrolyte was found to contain less than 0.25 PPM of lead, using the dithizone extraction analytical method.

6. Current Contacts

The use of the tantalum base as current carrier to the lead dioxide in the chlorate-perchlorate cell resulted in anode heating with even moderate currents. The use of metal pressure plates and clamps as current contacts against the lead dioxide proved inadequate in preventing heating in the contact area.

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Current contacts were also formed by embedding nickel wire in the upper part of the massive lead dioxide and by casting a low melting point alloy with embedded conducting wire about the top of the lead dioxide electrodes. A number of electrodes using these contacts operated at 3 to 10 amperes without local heating. Others failed after short periods in the chlorate-perchlorate cell.

Finally, the metal spray technique was used for forming a current contact area on lead dioxide electrodes. Only sprayed silver, of all metals tested, showed a low metal to lead dioxide contact resistance. As a result of this, a workable current contact was developed which consisted of a spray coating of silver (.001 inch thick), covered with a spray coating of copper, 1/8 inch thick or more.

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II. Miscellaneous Anode Materials

A. Previous Work

The following anode materials were found to be satisfactory in the work done in 1951 and 1952:

1. Tantalum carbide containing 17% platinum by weight.
2. Platinum-plated tantalum sheet.
3. The mineral plattnerite, a naturally occurring massive lead dioxide.

B. Promising Materials in 1953 and 1954

Of the materials tested during 1953 and 1954, the platinum-palladium alloys with high platinum content showed promise with low erosion rates. Appreciable erosion losses were observed with platinum-ruthenium and palladium-ruthenium alloys. Manganite ($Mn_2O_3 \cdot H_2O$) showed very little erosion but further work is necessary to ascertain its value.

C. Unsatisfactory Miscellaneous Materials Tested

The following materials were unsatisfactory for reasons outlined below:

1. Samples of bearing materials (carbon impregnated with various metals), silicon ferrite, impervious graphite, natural graphite, gold and silver were found to erode rapidly.

2. A nickel ferrite boule showed no appreciable erosion, but conversion of chlorate to perchlorate was very low.

3. Polished plate glass samples with a conductive film on one side failed rapidly.

4. Of three different samples of tin oxide blocks, one showed no appreciable erosion with operation at about 50% current efficiency.

5. Samples of conducting glasses and refractories either eroded or operated at a very high cell voltage.

6. Samples of pressed and fired mixtures of lead dioxide and magnetite showed considerable mechanical disintegration.

7. Several thousand mineral specimens were screened and 83 tested for electrical conductivity. The following more conductive ones were selected for cell testing: cassiterite (SnO_2), psilomelane ($BaMn_2Mn_8O_{16}(OH)_4$), ilmenite ($FeTiO_3$), hematite (Fe_2O_3), pyrolusite (MnO_2), and zincite (ZnO). All failed because of rapid erosion, high contact resistance or polarization.

8. A good plate of manganese dioxide was not obtained from either a manganese sulfate or manganese nitrate plating bath. The conductivity of the manganese dioxide was poor as compared to lead dioxide.

III. Silicon-Silicon Carbide

A. Number of Materials Tested

A total of 362 samples representing 140 different kinds of silicon-silicon

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carbide compositions were received from The Carborundum Company (subcontractor on this project), and have been tested as anode material in the chlorate-perchlorate cell.

B. Performance

1. None of these Carborundum compositions proved satisfactory; most of the anode samples showed the spalling or polarization characteristic found before, and a few samples exhibited rapid erosion, as reported in Project NR 352-304/2-1-52.

2. The extruded Durby #2* composition quenched in molten lead and the 90% silicon-10% silicon carbide composition, previously reported as promising (Project NR 352-304/2-1-52), were investigated further and were found unsatisfactory after a few hours of operation.

3. Certain calcined materials impregnated with silicon, including tempered Masonite** board, Homasote** and Compreg**, were found to operate at a low voltage and to make perchlorate at a fair current efficiency. However, after a few hours of operation, these specimens slowly polarized.

Various other calcined Masonite materials impregnated with silicon operated at fair current efficiencies for short periods of time, but upon extended operation current efficiencies dropped to a low value. Some erosion was found with these materials.

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* Silicon carbide in a silicon matrix.
** Resin impregnated wood fiber products.

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CONCLUSIONS

1. A massive, electroformed lead dioxide electrode has been developed and demonstrated on a laboratory scale to be a practical substitute for the platinum anode in the electrolytic oxidation of sodium chlorate to perchlorate.

2. Tantalum is the most satisfactory of the many base materials tested for lead dioxide plating. Other materials, less expensive than tantalum, show promise. These include nickel and some of the non-eroding silicon-silicon carbide compositions.

3. Massive lead dioxide generates perchlorate at a good current efficiency and with very little erosion. It has excellent electrical conductivity, and with the sprayed silver terminals which were devised, practical current contacts are obtained. The material, as developed in this research, has excellent mechanical strength and can be shaped by precision grinding.

4. The lead dioxide anode is believed ready for pilot plant testing in commercial size chlorate-perchlorate cells.

5. To perfect the anode for optimum serviceability, additional laboratory development work is necessary on anode base materials, lead dioxide conditioning and chlorate-perchlorate cell additives. This work can be run concurrently with pilot plant testing of the present anode.

6. Some platinum alloys produce perchlorates effectively, making further study of these as substitutes for pure platinum desirable.

7. All silicon-silicon carbide compositions tested to date are unsatisfactory as anode materials in the chlorate-perchlorate cell.

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RECOMMENDATIONS

1. Pilot plant testing of the massive lead dioxide anode in commercial sized cells should be initiated, to run concurrently with additional laboratory development work.

2. The testing of miscellaneous anode materials submitted for evaluation should be continued. These tests should include tin oxide, manganese oxides, and certain platinum alloys.

3. The testing of silicon-silicon carbide compositions as anode materials should be discontinued.

A. Lead Dioxide, Including Massive Plates

1. Summary of Previous Work Done Under 1951 Project NR 352-263/2-19-51 and 1952 Project NR 352-304/2-1-52

In 1951 lead dioxide plating was attempted from the following baths: lead nitrate, lead nitrate and aluminum nitrate, lead acetate, and alkaline lead tartrate. No satisfactory adherent deposit of lead dioxide could be made on steel from a lead nitrate bath. Several baths based on lead acetate proved unsatisfactory for plating on steel, Monel, nickel or tantalum sheet. Addition of gelatine to the plating baths did not seem beneficial at the low current densities used. An alkaline lead tartrate plating bath was developed to give adherent deposits of lead dioxide on the above base metals. A few screening tests of lead dioxide plated electrodes were carried out in a small beaker chlorate-perchlorate cell without conclusive results.

In 1952 anodes of electrodeposited lead dioxide on base materials, such as Monel, nickel and steel, which are themselves easily eroded in the chlorate-perchlorate cell, did not seem practical, since the base material was rapidly disintegrated as soon as the continuity of the lead dioxide was broken, even at a pinpoint. Brief attempts to prepare a pure electrodeposited lead dioxide anode by depositing a heavy coat of lead dioxide on copper and steel and then dissolving away the base metal with nitric and hydrochloric acids respectively were unsuccessful due to simultaneous attack on the lead dioxide.

Several baths were developed for plating lead dioxide on a tantalum base. Tantalum passes current anodically during lead dioxide plating. However, it immediately polarizes anodically in most other electrolytes, including that of the chlorate-perchlorate cell. Therefore, it acts as an inert, non-eroding electrode base in the chlorate-perchlorate cell. The baths from which the highest quality lead dioxide deposits on tantalum could be obtained were an alkaline lead tartrate (#7d), lead nitrate (#LN-2) and lead perchlorate (#LP-1). Compositions of these baths are given in Table I.* The life of lead dioxide plated tantalum anodes in the chlorate-perchlorate cell varied widely and erratically. In most cases, the anodes failed due to the lead dioxide falling loose rather than smoothly eroding. The maximum chlorate-perchlorate cell life of these lead dioxide coatings, which varied in thickness from 0.002 to 0.008 inches, was eight days.

Lead dioxide was readily plated on Durhy #2 base (see Section C-1) and on a synthetic magnetite base. A preliminary testing of these plated anodes in the chlorate-perchlorate cell gave sufficient promise to warrant further study. Deposition of lead dioxide on Durhy #1 base (Section C-1) could not be satisfactorily accomplished.

A smooth, adherent electrodeposit of lead dioxide on cast silicon was easily obtained, and the electrode operated smoothly in the

* NOTE: Because of the many tables of data resulting from this investigation, all the tables have been assembled at the end of this report so that the continuity of the text is not unduly disrupted.

chlorate-perchlorate cell until the silicon shattered as the continuity of the thin lead dioxide deposit was broken.

Plattnerite, a rare, naturally occurring massive lead dioxide, operated smoothly as anode in the chlorate-perchlorate cell at a low voltage without shattering and with very little erosion.

2. Work Done in 1953 and 1954

Continued plating and testing of relatively thin lead dioxide coatings (about 0.01 inch maximum thickness), on tantalum produced the same erratic results as noted in 1952. One electrode ran for 12.2 days in the chlorate-perchlorate cell at a current density of 0.1 amp./cm.^{2}, with an efficiency of 48.9 per cent. A number of other electrodes plated in the same manner operated for as short a time as a few hours before failure by tantalum polarization and a breaking apart of the lead dioxide coating.

a. Plating Massive Lead Dioxide

In view of the promising results obtained in a preliminary test of a naturally occurring massive lead dioxide as anode in the chlorate-perchlorate cell, effort was concentrated on electroplating lead dioxide in massive forms on various base metals. Table II shows in detail the plating conditions for these massive electrodes including types of base materials and thicknesses and weights of deposits. First efforts were directed toward plating the lead dioxide on only one side of a flat base metal by blanking off the edges and back with inert material such as Plexiglas. It was hoped to strip away the base metal backing to produce a pure massive lead dioxide anode. After plating electrodes 191A to D (Table II), the deposition of lead dioxide on only one side of a base metal was abandoned due to the brittleness of the lead dioxide and the failure of the blanking jig; the lead dioxide grew in large nodules along the base metal edge around the sides of the jig and also through sealed jig joints.

Heavy electrodeposits of lead dioxide were readily made on tantalum rod without any nodular growth or treeing in the LN-2 bath at current densities of 15-30 amps./ft.^{2} and a temperature of 70°C. Massive lead dioxide deposits were also made on flat rectangular sections of Monel screen, nickel screen and tantalum sheet, gauze and screen. In these cases, there was some nodular growth at the edges which could be cut away on a diamond-edged circular saw or ground down on an abrasive wheel. It was later found that practically all of the nodular growth and treeing of lead dioxide on flat electrodes could be eliminated by the use of suitable baffles surrounding the anode, especially along the side and bottom edges. These baffles were constructed of clear Plexiglas to permit observation of anode growth during the lead dioxide deposition. Plexiglas was found to be unaffected by immersion in the hot lead nitrate plating bath.

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Large, Rectangular Lead Dioxide Electrodes

The largest lead dioxide electrodes formed to date were on tantalum screen (14 mesh, 0.025" wire), tantalum sheet (.003" thick), and nickel screen (16 mesh, .012" wire). These massive lead dioxide electrodes measured 15-1/2" long by 3-1/2" wide, and about 3/4" thick, examples of which are electrodes numbered 219,236 and 238 in Table II.

Electrode #238 with a nickel screen base whose cost is less than 1% that of tantalum screen is illustrated in Figures 1 and 2. Plating of similar massive lead dioxide electrodes on steel screen base were planned but not completed in this period. As previously noted, base materials, such as nickel and steel, are rapidly eroded when the lead dioxide electrode is operated anodically in the chlorate-perchlorate cell. It is thought that this disadvantage can be overcome by either preconditioning the lead dioxide electrolytically in sodium chlorate electrolyte until all the base metal is leached out, or by removing the eroded metal base from the electrolyte during normal operation as an insoluble hydroxide residue at an alkaline pH.

The use of thin tantalum sheet resulted in a reduction of starting sheet cost to 15% that of the tantalum screen. However, the lead dioxide electroformed on sheet was weaker than that formed on screen, which permitted binding of the lead dioxide through the closely spaced open screen areas. Punching of the sheet with small closely spaced holes was not satisfactory, since the lead dioxide formed in heavy nodules at the sharp edges of the holes. Before attempting plating of lead dioxide on thin, rolled tantalum sheet, it was necessary to remove the invisible film of oxide present by vigorous abrasion with fine emery and crocus cloths; otherwise, the sheet tantalum would polarize in the plating bath. A similar polarization was encountered on attempting to plate lead dioxide on 16 gauge tantalum wire.

When plating lead dioxide on base materials which were not rigid, such as fine mesh screening or thin metal sheet, it was necessary to draw such base materials taut within the plastic shield used to baffle the edges. This was done by attaching strong threads from the bottom of the plating base to the bottom of the plastic shield. This prevented flexing or bending of the metal base during the early stages of the lead dioxide plating before the lead dioxide had grown heavy enough to resist such bending. Vinyon thread was found to be strong and inert to the plating solution.

Lead Dioxide Plated on Nickel Wire

Rods of lead dioxide up to 1-1/8 inches in diameter and 13 inches long were conveniently electrodeposited on nickel wire of number 16 to 22 gauge in the lead nitrate bath. The wires, suspended vertically in the plating bath, were

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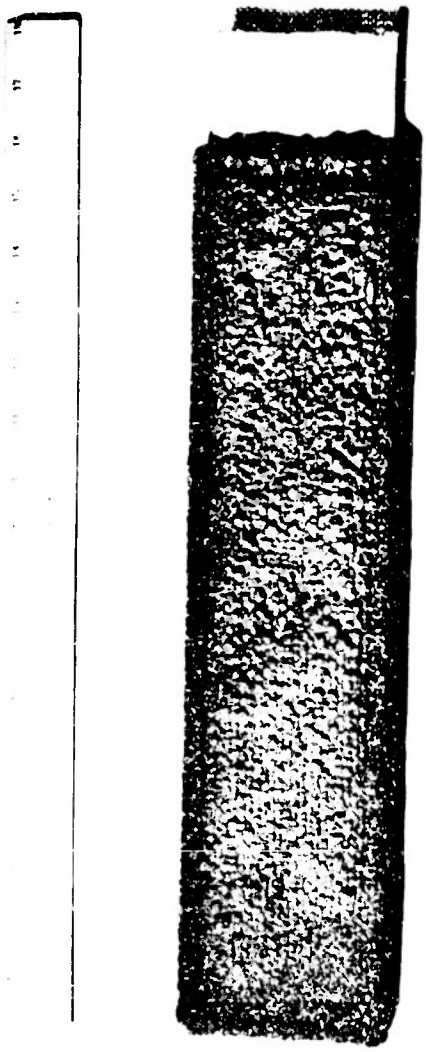

FIGURE 1 - Electrode No. 238, Lead Dioxide Electroformed on Nickel Screen - Face View

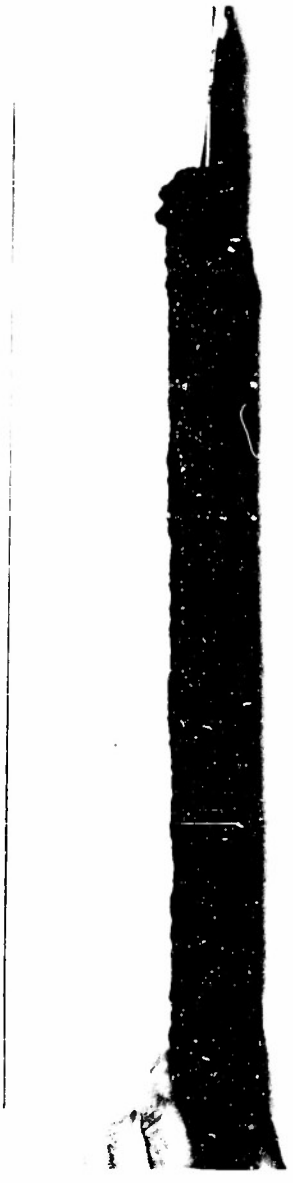

FIGURE 2 - Electrode No. 238, Lead Dioxide Electroformed on Nickel Screen - Edge View

maintained taut by hanging a mercury weighted glass bulb from a loop on the lower end. The loop on the wire was covered with a stop-off lacquer. On removal from the plating bath and after cutting off the lower one-half inch of the lead dioxide rod, the nickel wire core could be removed by a moderate pull with pliers on the upper end. These lead dioxide rods were used in current contact studies to be described in a later paragraph, and they are also necessary in the measurement of the temperature coefficient of thermal expansion for which arrangements were planned. A lead dioxide rod of this type is illustrated in Figure 3.

Lead Dioxide Plated on Non-Metallic Base Materials

Lead dioxide was plated from the lead nitrate bath on several samples of untempered Masonite, calcined and impregnated with silicon, which were received from Carborundum Company. In all cases, there was considerable gassing at the anode resulting in the formation of a lead dioxide deposit having many gas holes and vertical crevices. The base also showed erosion from plating bath action.

Several samples of graphite and carbon were received from National Carbon Company for testing as base material for electrodeposited lead dioxide from a lead nitrate plating bath. On AGX graphite, the lead dioxide deposit was discontinuous and formed in closely spaced needles or spikes. There was considerable anodic gassing during plating. No lead dioxide was anodically deposited on CK-3 carbon which was seriously eroded in the plating bath. A yellow slime which appeared to be lead monoxide was formed on the carbon. Reuter, Fostoria molded graphite gave results similar to that obtained with AGX graphite. In addition, a viscous syrup was leached from the graphite. The quality of the lead dioxide deposit on spectrographic grade graphite rod was about equal to that on tantalum rod. However, some shallow crevices were formed on the lower end of one rod due to concentrated anodic gassing in this area. Several Grade AUC National graphite rods, 1/4 inch diameter, which were reported to be the closest industrial equivalent of spectrographic grade graphite, were received too late to be tested as a lead dioxide plating base.

Lead dioxide was also plated from the lead nitrate bath on No. 10-8 Durhy #2 extruded stock, 7/16 inch in diameter. A hard lead dioxide deposit was formed to a total diameter of 3/4 inch as illustrated in Figure 4. This lead dioxide surface was cross marked with closely spaced fissures due to similar surface grooves in the Durhy starting rod.

Lead Dioxide on Silver

Upon attempting lead dioxide plating on a silver wire base from a lead nitrate bath, the silver was etched and eroded, and no lead dioxide was deposited.

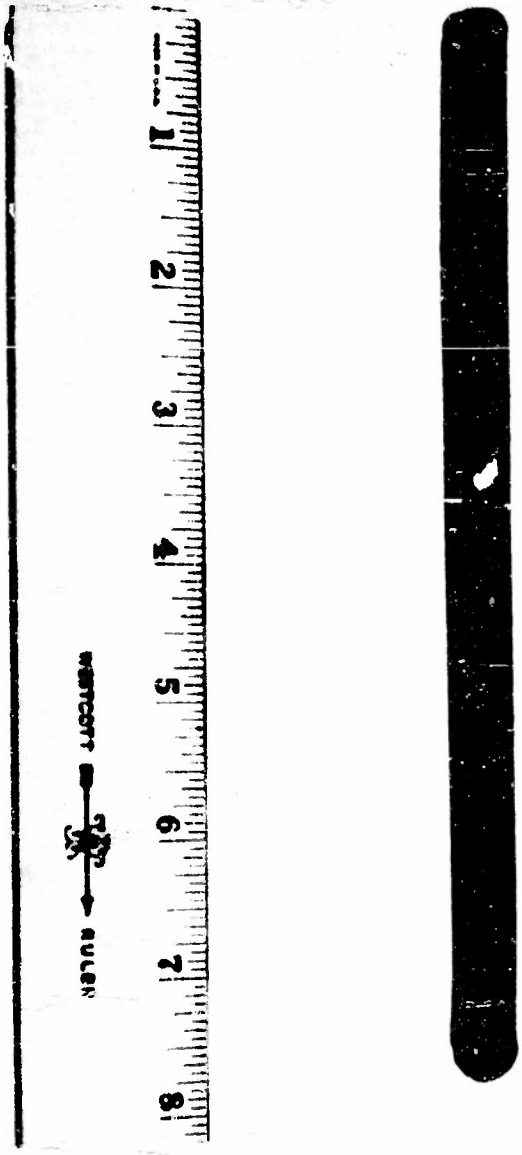

FIGURE 3 - Lead Dioxide Rod Formed on Nickel Wire

(Note: Nickel wire core (#20 B&S gauge) was withdrawn prior to this picture.)

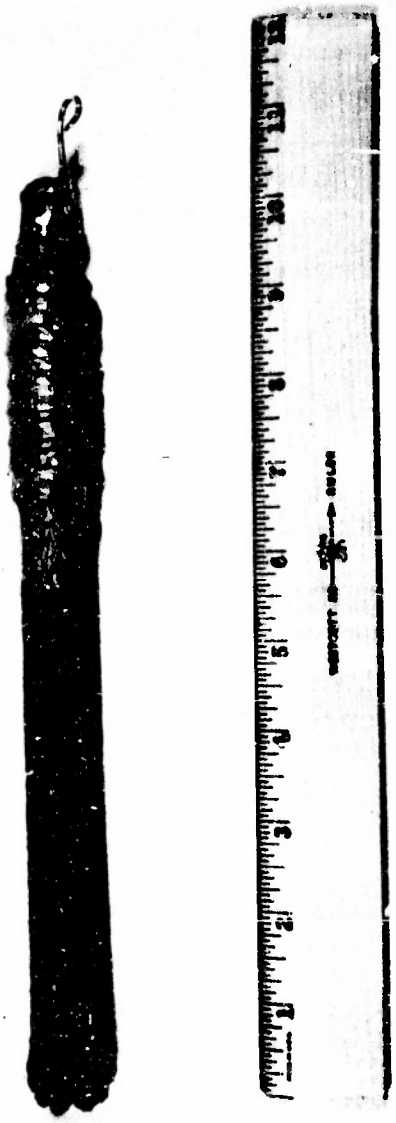

FIGURE 4 - Lead Dioxide Plated on Durhy #2 Rod

(Note: The current contact at the top of the electrode consists of sprayed coatings of silver and copper. No. 12 copper wire is spirally wound over the sprayed copper, and soft soldered to it. The entire area is finally coated with stop-off lacquer for corrosion resistance.)

Plating Bath, Operation, Composition and Additives

During the plating operations it was found that the addition of about 0.5 g./l. of copper nitrate, Cu $(NO_3)_2 \cdot 3H_2O$, to the LM-2 bath was sufficient to prevent plating of lead on the graphite cathodes. The addition of 0.5 to 0.75 g./l. of gelatin to the LM-2 bath had a pronounced effect in reducing the graininess of the lead dioxide. However, the massive deposit had a much lower fracturing strength as compared to that plated from a gelatin-free bath. Rods of lead dioxide plated on nickel wire from a gelatin-containing lead nitrate bath when broken open revealed many fine cracks radiating from the center to almost the outside circumference of 1/2 inch diameter pieces. Also, under certain conditions when plating lead dioxide from such a bath, anodic gassing occurred which caused the formation of small pockets, lumps, and general irregularity in the lead dioxide surface. Because of the erratic results obtained by the addition of the natural product, gelatin, to the plating bath, a brief study was made of synthetic surface-active agents. A large number were eliminated from experimental consideration because of their known instability in electrolytes and acid solution, and insolubility at elevated temperatures. Representative examples of cationic, anionic and non-ionic surface-active agents were then tested for stability in the lead nitrate plating bath up to 95°C., and for effectiveness in producing a fine-grained lead dioxide deposit with maximum strength and density. Igepal CO-880, a non-ionic agent manufactured by Antara Chemical Division of General Dyestuff Corporation was considered the most effective, and incorperated into the lead nitrate bath at 0.75 grams per liter. The concentration of copper nitrate trihydrate addition was also standardized at 0.75 grams per liter. Detailed results of the surface active agent tests are given in Table III.

Extended experience has confirmed the observation that the efficiency of lead dioxide plating from the several plating baths used is practically 100 percent with a freshly prepared or replenished bath. Litharge, PbO, was used to replenish the lead in the lead nitrate bath. Reagent grade lead oxide, PbO was used in preparing and replenishing small plating baths of up to three liters, and technical grade lead oxide was used for larger 30 liter plating baths, with no noticeable difference in the quality of the electrodeposited lead dioxide. Some nitric acid was also lost from the lead nitrate bath during plating, and was added when the bath was replenished with litharge, to maintain the desired pH. It has been found desirable to adjust the initial pH of the lead nitrate bath to about 2.8, and operate in the pH range of 0.8 to 2.8 during lead dioxide deposition. In the pH range above 3.5, there was the likelihood of the formation of an electrical insulating film or glaze of lower lead oxides on the cathodes, and at pH values below 0.8, acid fuming from the plating bath became excessive at 70°C.

Small plating baths of up to three liters capacity were replenished batch-wise at the conclusion of each lead dioxide electrode plating. Baths of 30 liter capacity, used for plating larger lead dioxide electrodes, were continuously replenished with lead oxide. The plating solution was pumped through another vessel heated to the plating bath temperature, and containing a filter bed of glass wool and glass beads of 3 to 5 mm. diameter, and the lead oxide was dispersed in this solution above the filter bed. The depleted plating solution entered the replenishing vessel at the top by a siphon arrangement, gradually dissolved the lead oxide, passed through the filter bed, and was pumped out of the bottom to the plating vessel. Nitric acid, when necessary, was also added to the replenishing bath to avoid sudden pH changes in the plating bath. The replenishing system could be operated continuously or only at intervals when the depletion rate was slow. The lead nitrate concentration of the plating baths was determined in two ways, first, by a continuous material balance on lead oxide added and lead dioxide removed, and second, by a determination of solids content at intervals. A 10 ml. sample was evaporated to dryness at 110°C. and weighed, neglecting the presence of the small amount of addition agents.

The lead tartrate and lead perchlorate plating baths have a much lower lead concentration than the lead nitrate bath. Therefore, they were reformulated to a higher concentration (Table I), and their efficiency in lead dioxide plating studied. At 70°C., the concentrated lead tartrate bath gave lustrous adherent deposits at anode current densities up to 10 amp./ft.^{2}. For the concentrated lead perchlorate bath, an anode current density of 20 amp./ft.^{2} and an initial pH of 1.5-2 at 70°C. were found desirable for a smooth, adherent lead dioxide deposit. These baths were found to be sensitive to pH changes, and susceptible to precipitation of solids during plating.

The most satisfactory method found for precleaning of anode base materials prior to lead dioxide plating was to remove surface dirt and grease, etc. with petroleum ether, followed in some cases with a steam cleaning and drying. Cathodes of graphite or carbon were used in the plating bath, and it was found that anodic treeing could be minimized by keeping the lower end of the cathodes at or above the lower end of the anode. A stop-off lacquer was applied to those portions of the anode base materials which it was desired to keep free of lead dioxide deposit. This was "Micro Stop-Off Lacquer, HR-302" manufactured by Michigan Chrome and Chemical Company. When plating on a flat base, at constant current, the area and thus the current density did not change appreciably. However, when plating on rod or wire, it was necessary to increase the current in finite steps to maintain approximately constant current density.

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Analysis of Massive Lead Dioxide

X-ray diffraction and spectrographic analyses were made of portions of several of the massive lead dioxide deposits, and the results are detailed in Table IV. In all cases, the deposit was identified as PbO_2, with lead as the only major spectrographic constituent. The minor constituents were not especially significant, but it was noted that nickel appeared when the deposit was made on Monel screen or on tantalum rod with a nickel wire coiled about the upper end. Also, copper appeared when the plating bath contained 0.5 g./l. or more of copper nitrate.

b. Testing Massive Lead Dioxide Electrodes

A number of changes were made in the procedure for testing the above massive lead dioxide anodes in the chlorate-perchlorate cell as compared to that followed with thin electrodeposits of lead dioxide in 1952. In some cases, the cells were cooled by partial immersion directly into a refrigerated bath instead of circulating coolant through glass coils, immersed in the cells. Cell currents were maintained constant as before by means of electronic controllers. Glass was substituted for stainless steel stirring rods on the motor stirrers because of poor electrical shielding from the motor. Some of the later testing was carried out without any stirring of the electrolyte. Current efficiencies were not noticeably affected by this change. It was found unnecessary to provide any surface protection for the massive lead dioxide anodes such as a Silicone grease coating or Tygon sleeves at the liquid-air interface, which had been used to prolong the cell life of thin lead dioxide electrodeposits. Type 430 stainless steel cathodes were found satisfactory and eliminated the rust discoloration of the electrolyte resulting when ordinary carbon steel cathodes were used. A 10 ampere cell with lead dioxide anode is shown in Figure 5.

Table V lists the individual current efficiencies obtained with massive lead dioxide anodes in the chlorate-perchlorate cell. The electrolysis was carried out batch-wise at 3 to 10 amperes in cells containing 1.0 to 1.2 liters of a 600 to 630 g./l. sodium chlorate solution. Electrode 200 was operated at 25 amperes in a cell containing 5 liters of sodium chlorate solution. The degree of conversion of chlorate to perchlorate was checked at 6 to 24 hour intervals by volumetric analysis of a small aliquot for oxidizing power by the bromide-iodide-thiosulfate method. This was frequently checked by analysis of final cell electrolyte for sodium perchlorate, and the two methods were found to agree within ± 3 percent. In most cases, the electrolysis was continued to reduce the chlorate content below 100 g./l. The product solution was then removed, the cell replenished with fresh sodium chlorate solution, and the testing of the lead dioxide anode in chlorate-perchlorate electrolysis continued.

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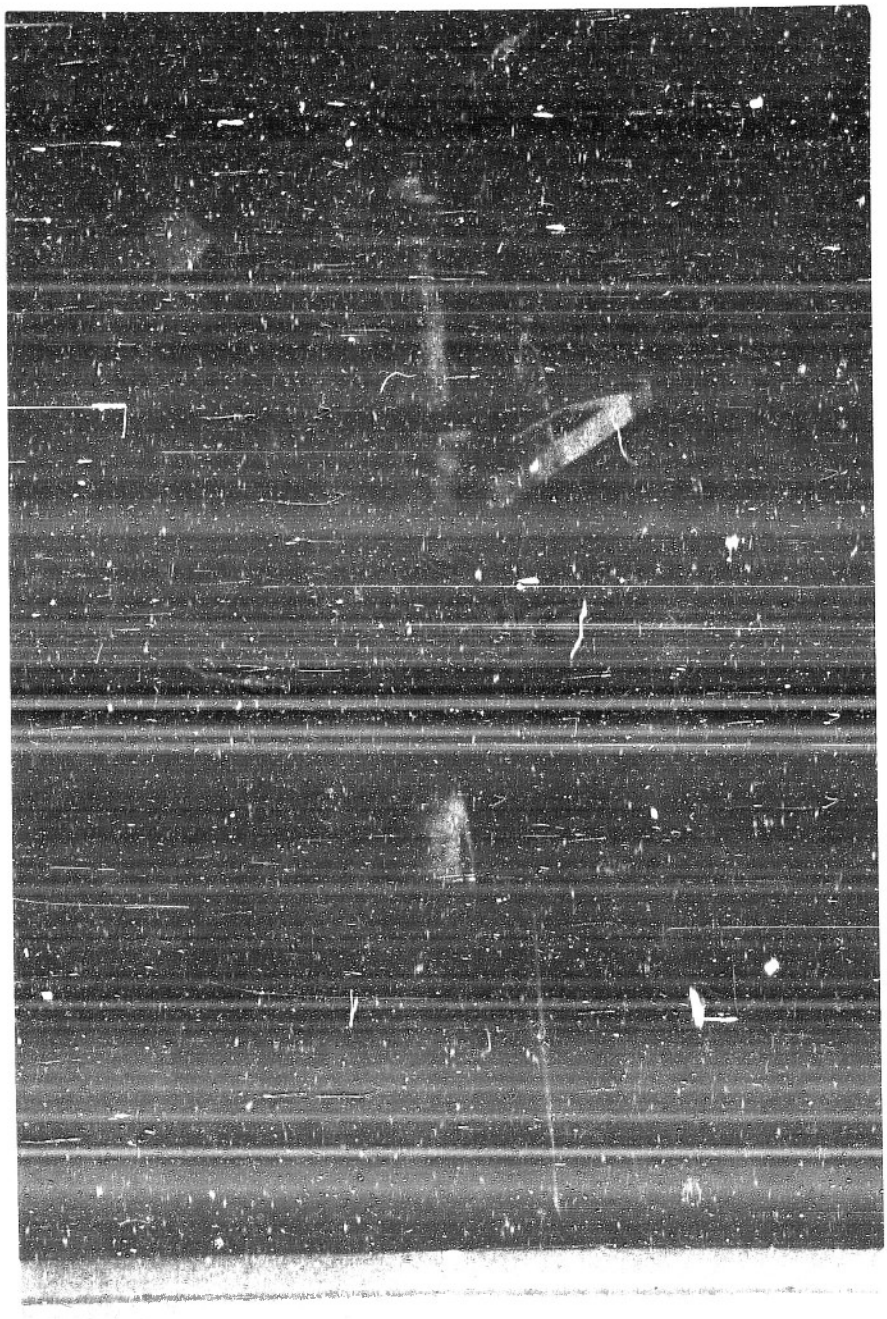

FIGURE 5 - Ten Ampere Cell With Lead Dioxide Anode

The loss of water by evaporation and electrolysis from a ten ampere chlorate-perchlorate cell containing 1200 ml. of electrolyte was about 0.35 ml. per ampere-hour or 80 ml. a day. This was corrected one or more times each day by addition of distilled water to bring the cell electrolyte back to the original level. All lead dioxide electrodes from Number 214 on were coated with a stop-off lacquer* over the current contact area above the electrolyte level to prevent electrolyte mist corrosion in the chlorate-perchlorate cell.

Current Efficiency with Lead Dioxide Anode

These massive lead dioxide anodes were operated at current densities of 0.1 to 0.45 amp./cm.^{2}, at cell temperatures of 5°-10°C. and 50°C., and in both acid and alkaline chlorate electrolyte. Current efficiencies were compared over the sodium chlorate concentration range of 600 to 100 g./l. Table VI, giving a summary of the current efficiency data of Table V, indicates that an anode current density of 0.1 amp./cm.^{2} is too low (53% ave. current eff.) for efficient operation of the lead dioxide electrode. At anode current densities of 0.2 and 0.3 amp./cm.^{2}, the average current efficiency was about 68% and seemed unaffected by cell temperature in the range of 5° to 50°C. At an anode current density of 0.45 amp./cm.^{2}, a higher current efficiency (78%) was found at 48°C. than at 15°C. (54%). These last results, however, are based on a small number of tests and need confirmation.

Cell current efficiency with the lead dioxide anode dropped sharply as the sodium chlorate was converted to perchlorate, as shown in Figures 6 and 7. At sodium chlorate concentrations of 600 to 450 g./l., current efficiencies above 90% have been noted. The current efficiency dropped below 25% as the sodium chlorate was consumed by electrolysis to concentrations below 100 g./l.

New lead dioxide anodes were found to operate at a somewhat lower current efficiency than after a period of aging of one or more batch electrolyses. When desired, the cells were operated in the acid range by manual addition of 0.5 normal perchloric acid as found necessary. In a few cases the cells maintained themselves in the acid range without perchloric acid addition, this being generally true after the anode had been conditioned by previous operation at low pH. Normally, the electrolyte pH rapidly rose to 9-10 and maintained itself in this range throughout the electrolysis.

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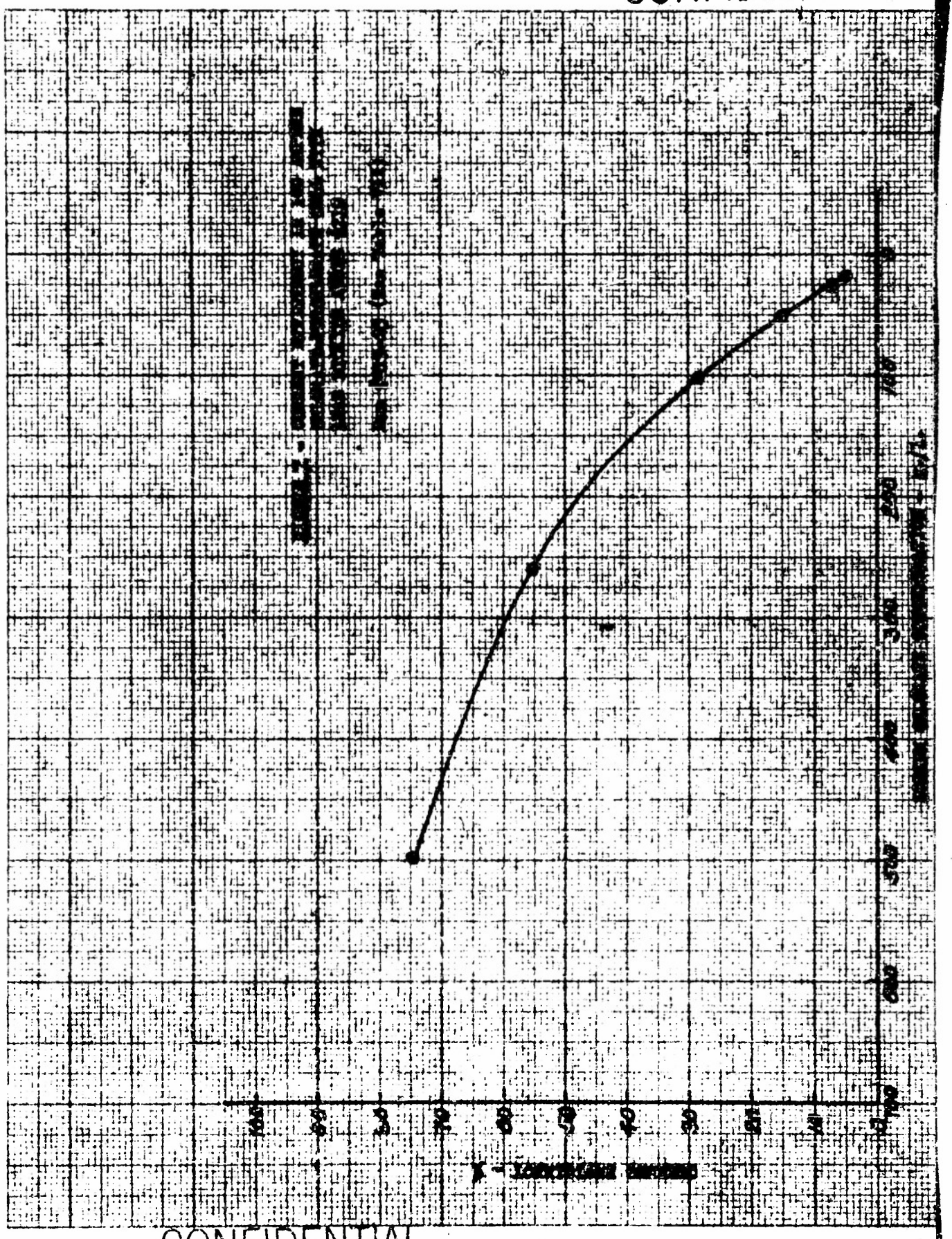
*Micro Stop-Off Lacquer, HR-302" - Michigan Chrome and Chemical Company

359-11 KEUFFEL & ESSER CO.
10 × 10 to the ½ inch, 5th lines accented.
MADE IN U.S.A.



Electrode 205 was formed by electrodepositing lead dioxide over a hollow tantalum U-tube. This anode was operated in the chlorate-perchlorate cell with 10°C. cooling water flowing through the core for the first two tests. Current efficiencies were not appreciably different from those of succeeding tests where only the electrolyte was cooled.

There seemed to be no appreciable effect of electrolyte pH in the range of 1 to 10 on current efficiency in any of the series of tests carried out in this laboratory. Providence College (1) has reported the measurement of potentials at the platinum anode during electrolysis of chlorate solution. From these results, it was speculated that at alkaline pH values (e.g. 9.7) both oxygen and perchlorate are being produced to an appreciable extent and that, therefore, the current efficiency for the production of perchlorate decreases with an increase in the pH in the alkaline range.

Current Efficiency with Platinum Anode

A 10 ampere platinum anode chlorate-perchlorate cell was operated at an anode current density of 0.3 amp./cm.^{2} and an electrolyte temperature of 45°C. The average current efficiency for three runs in the sodium chlorate concentration range of 600 to 100 g./l. was 89%, as compared to an average 68% with the lead dioxide anode. In one case, the sodium chlorate concentration was reduced to 4 g./l. with the platinum anode for an overall current efficiency of 80%. The electrolyte was allowed to maintain its pH at about 9 during these runs.

Current Efficiency with Lead Dioxide Anodes Formed on Non-Metallic Bases

Two massive lead dioxide electrodes, formed by plating over 1/4 inch diameter spectrographic grade graphite rod, were tested in the chlorate-perchlorate cell. One electrode (#220) failed during the first test. The lead dioxide was broken into long vertical splines, and the graphite base was swollen and eroded. However, the other electrode (#221) was operated smoothly for four batch electrolyses of sodium chlorate without any erosion or failure. The current efficiencies were equal to those obtained with lead dioxide over tantalum base anodes, as shown in Table V. Therefore, the failure of the first electrode was probably due to a crack or other original flaw in the lead dioxide.

Two lead dioxide electrodes (#222 and #230, Table V) plated on Durhy #2 rod were tested in the chlorate-perchlorate cell at 15 amperes and a current density of 0.3 amp./cm.^{2}. These anodes operated in a normal manner, and current efficiencies were about the same as those obtained with lead dioxide over tantalum base anodes.

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Effect of Cell Additives on Current Efficiency

Sodium fluoride addition to the sodium chlorate electrolyte at a concentration of 2.5 g./l. increased the overall current efficiency appreciably on the first batch electrolysis. However, this current efficiency steadily dropped on three succeeding electrolyses with lead dioxide anode #196 to below the value obtained before sodium fluoride addition. A similar effect was observed in two tests with electrode #227. Also, the type 430 stainless steel cathodes were etched and pitted in scattered areas above the solution. All glass surfaces were protected by a wax coating during these tests.

The presence of sodium dichromate at concentrations as low as 0.5 g./l. of the dihydrate sharply decreased the current efficiency when operating with a lead dioxide anode. In the case of lead dioxide electrode #223 (Table V), the addition of 5.0 g./l. of sodium dichromate to the electrolyte lowered the current efficiency in the sodium chlorate concentration range of 600 to 150 g./l. to 16%. A 100 ampere cell, details of which are given in a following paragraph, was operated with an electrolyte made with a technical grade sodium chlorate which contained 0.08% sodium dichromate, equivalent to a 0.5 g./l. concentration in the electrolyte. A current efficiency of 27% was obtained with this electrolyte in the sodium chlorate concentration range of 580 to 100 g./l. When a sodium chlorate solution containing 1.2 g./l. sodium dichromate was electrolyzed in this 100 ampere cell, the overall current efficiency from 600 to 100 g./l. sodium chlorate was 25%.

Sodium thiocyanate at a concentration of 1.0 g./l. did not seem to affect the current efficiency of a cell having a lead dioxide anode. These tests were made with electrode #226 (Table V).

A continuation of tests with cell additives to increase current efficiency was planned. This was to include further tests with sodium fluoride under various conditions.

c. 100 Ampere Cell with Lead Dioxide Anode

A suitable current contact was developed using sprayed silver and copper terminals, which would carry large currents to massive lead dioxide without local heating. This development made possible the operation of a 100 ampere chlorate-perchlorate cell with an electroformed lead dioxide anode (#219, Table II). A rectangular shaped glass jar of 6 liters capacity was used as the cell body and was operated with 5 liters of sodium chlorate electrolyte having an initial concentration of about 600 g./l. Other equipment details and operating conditions were similar to those described in other parts of this section for 10 ampere cells. Figure 8 shows this 100 ampere cell in operation.

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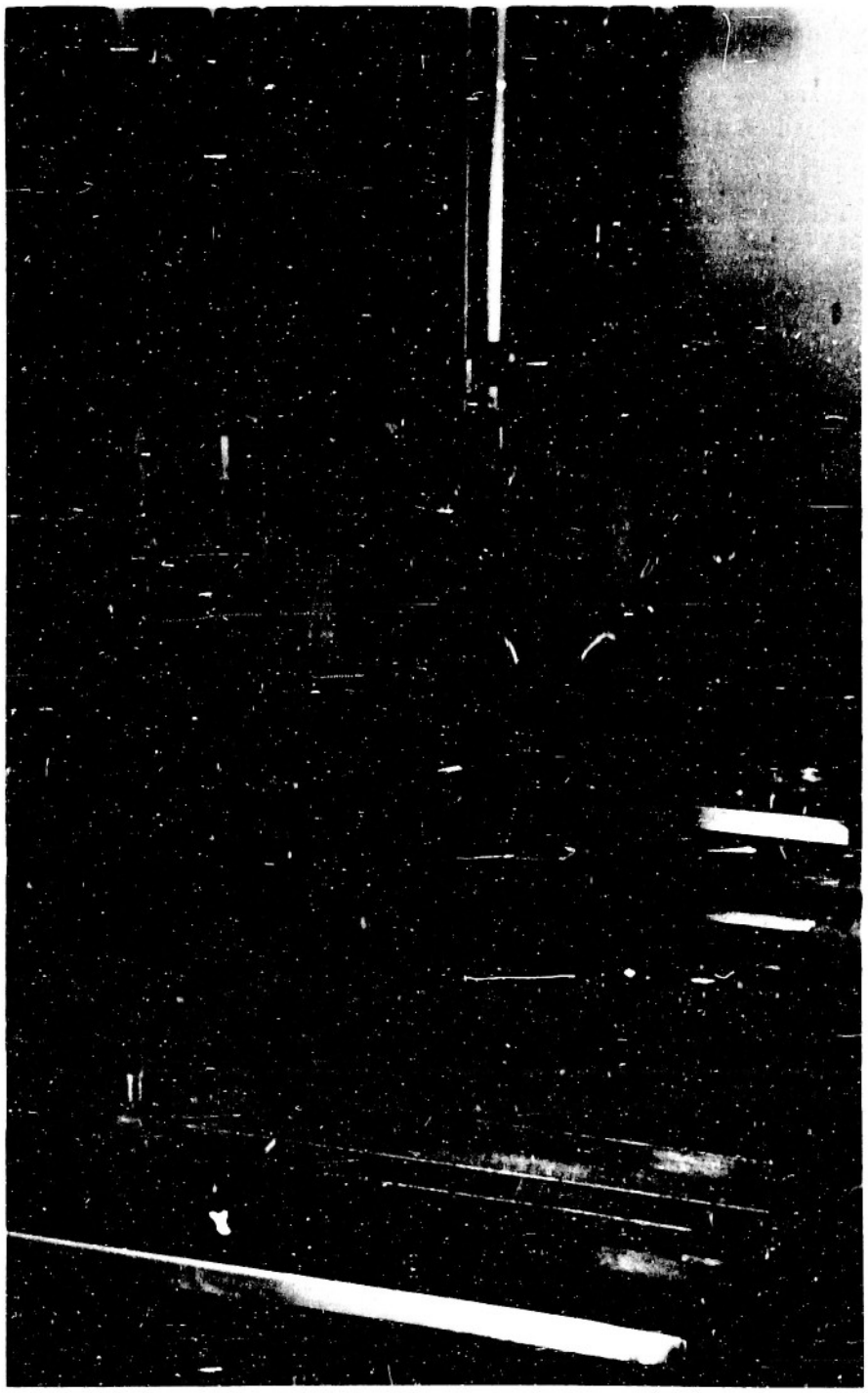

FIGURE 8

100 AMPERE CELL IN OPERATION WITH LEAD DIOXIDE ANODE #219

This cell was operated with the lead dioxide anode for 24 batch electrolyses of sodium chlorate to perchlorate for a total running time of 860 hours or 35.8 days without any noticeable erosion of the anode. Data, including current efficiencies on these runs are given in Table VII. The variation in current efficiency with decreasing sodium chlorate concentration during electrolysis is shown in Figure 7 for a typical run. In all but a few instances, the cell was run at 100 amperes, a current density of 0.28 amp./cm.^{2} and a temperature range of 30-50°C. Under these conditions, the average current efficiency in the sodium chlorate concentration range of 600 to 100 g./l. was about 47%.

The cell was then operated with a sodium chlorate solution containing sodium dichromate additive, which lowered the current efficiency to about 26% as described in the above section on additives. However, on succeeding electrolyses with dichromate-free sodium chlorate, the current efficiency was raised to an average 61%. This indicates a possible conditioning action on the lead dioxide anode by the sodium dichromate.

Insertion of inert baffles between the anode and cathodes of the 100 ampere cell resulted in some rise in the current efficiency, but also a doubling in the cell voltage and in power consumption.

d. Weight Losses of Lead Dioxide Anodes in Chlorate Electrolysis

The appearance of the lead dioxide anodes after testing in the chlorate-perchlorate cells was essentially unchanged. There was no localized or serious erosion or cracking of the lead dioxide deposit. In general, the peaks of the surface lead dioxide crystals lost their metallic luster, and under the microscope a smoothing of the points was apparent. Otherwise, there was no attack on the anode. The electrolyte in all cases remained clear and colorless, except where discoloration occurred due to corrosion of auxiliary cell components other than the lead dioxide anode.

Weight losses of lead dioxide anodes in laboratory scale chlorate-perchlorate cells corresponded to a maximum of about 50 grams per ton of sodium perchlorate formed. In most cases, there was either no detectable weight loss or the weight loss was smaller than the maximum noted. Losses in platinum cells have been reported (2) to be 0.2 troy ounce (6.2 g.) per ton of sodium perchlorate formed. Therefore, lead dioxide anode weight losses might be considered to compare favorably with those of platinum anodes, especially on a cost basis. Lead dioxide weight loss studies are summarized in Table VIII. These lead dioxide electrodes were cell tested for periods corresponding to up to 60 days continuous operation.

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e. Lead Pick-Up by Electrolytic Sodium Perchlorate

In view of the concern expressed over possible lead contamination of perchlorate from a cell using a lead dioxide anode, a spectrographic study was made of the product electrolyte. A spectrogram of evaporated electrolyte from a chlorate-perchlorate cell after 28 hours operation at 5.8 amperes with a lead dioxide filled storage battery plate showed no evidence of lead, although there was considerable erosion of lead from the plate. Spectrograms of cathode scum and insoluble cell liquor precipitate, obtained after operating cell #194-1 (See Tables II and V) for five days at 5 amperes with an electrodeposited massive lead dioxide anode, showed lead as a minor constituent. The evaporated electrolyte from the same cell revealed no spectrographic tract of lead. Thus, the eroded lead from the anode either plated out on the cathode or formed an insoluble compound. The 100 ampere cell in one instance (#219-2, Table VII) was run until all the chlorate had been converted to perchlorate, and the dried sodium perchlorate was analyzed for lead by the dithizone extraction method. Only 0.25 P.P.M. lead was found.

f. Current Contact to Lead Dioxide

Due to relatively high contact resistance of lead dioxide, the contriving of a workable, non-heating lead dioxide current contact has taken considerable research effort. Tables IX and X list the various methods used to bring current into the massive lead dioxide electrodes. The use of metal pressure plates and clamps against the outside surface of the lead dioxide proved inadequate in preventing heating in the contact area with even moderate currents.

Casting of a low melting alloy such as Wood's metal (m.p. 70°C.) around the upper end of a lead dioxide anode, which had already been closely wrapped with copper or nickel wire to serve as current leads proved more satisfactory. This type of contact, however, was somewhat bulky and it was necessary to protect the surface of the metal casting from immersion or spray contact with the chlorate-perchlorate cell electrolyte to prevent serious corrosion. Also, the Wood's metal did not wet the lead dioxide surface well, and so the contact was not dependable. In at least one case, the electrode became warm due to poor current contact, and a portion of the Wood's metal was melted, falling into the cell. Electrode 200 was first spray coated with zinc metal over the top two inches to a thickness of about 0.005 inches. Cast Wood's metal then wet and adhered tightly to this zinc coating.

A fairly satisfactory current contact consisted of massive lead dioxide plated over a base assembly composed of nickel wire tightly wound around or otherwise attached to the upper end of tantalum rod, plate or screen. The portion of the electrode containing the embedded nickel wire remained above the electrolyte level in the chlorate-perchlorate cell. On the finished electrode, the free ends of the nickel wire served to carry the current into the lead dioxide. Thus, the tantalum served only as a supporting base and current carrier during plating, since it gradually heated up when carrying even moderate currents in the chlorate-perchlorate cell. However, there was a tendency for more or less erosion of the nickel wire in the lead nitrate plating bath. During plating, the lead dioxide formed more heavily on the nickel than on tantalum in the same area, resulting in nodular growth and uneven thicknesses on heavy lead dioxide deposits. These disadvantages were minor when plating on solid tantalum rod, but became serious when using flat tantalum sheet or screen. When copper wire was used in place of nickel it rapidly eroded in the lead nitrate bath, and no lead dioxide was deposited.

Electrode 200 mentioned in the second paragraph above depended on two current contact methods for carrying current to the lead dioxide during testing in the chlorate-perchlorate cell. It contained nickel wires embedded in the lead dioxide, with the free wire ends turned over and embedded in the Wood's metal casting. This electrode was operated at 25 amperes at an anode current density of 0.2 amp./cm.^{2}, with current contact made to the exposed loops of nickel wire. The anode ran cool and a current efficiency of 78% was attained.

When massive lead dioxide was plated over Monel screen (Plate #194, Table II), the Monel carried current into the lead dioxide during operation in the chlorate-perchlorate cell. However, when the electrode was broken open after 11 days' operation at 5 amperes, it was found that the Monel screen base had completely eroded away below the electrolyte level, leaving voids in the lead dioxide. On spectrographic analysis of the precipitate from the above cell liquors, nickel was found to be a major constituent and copper a minor constituent. The current efficiency was lower than with a tantalum base anode.

Several attempts were made to carry the chlorate-perchlorate cell current to the lead dioxide directly through the tantalum base. In every case, whether the base was rod or screen, the anode rapidly became hot, and surface temperatures of 100°C. were measured with a thermocouple contact.

Some promising work has been done on the use of the metal spray technique for forming adherent metallic deposits over lead dioxide for use as low resistance current contacts. In one method, the spraying was done with a "Metco" spray gun into which was fed 1/8 inch diameter wire. Coatings of zinc, lead, copper, tin, silver, and aluminum were sprayed on 1/4 inch diameter lead dioxide rods both singly and in double layers of different metals. The potential across the metal to lead dioxide contact area was measured on a potentiometer with 0.5 ampere passing through the lead dioxide specimen rod. Voltage drops were all in the range of 0.5 to 1.5 volts except in the case of silver on lead dioxide which was 0.002 volts.

This series of metal sprayings was repeated, with great care being taken to avoid heating the lead dioxide much above 100°C. during the metal spraying. The potentials across the metal to lead dioxide contact areas were measured as above, but with one ampere passing so that the measured potentials were numerically equal to the contact resistance in ohms. In all cases where silver was the base coating, the metal to lead dioxide potential drops were about .0002 volt. Other metals gave potential drops of about 0.15 volt.

Spray coating of various metals on massive lead dioxide was also done by the Colmonoy Sprayweld Process. By this method, powdered metal was air propelled through the jet of a gun where it was heated to incandescence by an oxygen-acetylene flame and projected by compressed air to the surface to be coated. A silver to lead dioxide coating formed in this way had a potential drop of 0.0002 volt at one ampere. Other metals showed potential drops of 0.6 to 1.5 volts, except copper which was 0.03 volt.

By comparison, nickel wire embedded in massive lead dioxide during electroforming showed a metal to lead dioxide potential drop of 0.025 volt at one ampere. The contact resistance is thus about 100 times greater than that of sprayed silver to lead dioxide.

On the basis of these results, it was concluded that silver is the only practical metal of those tested for use as a first spray coat over lead dioxide for low contact resistance. Also, any other good conductor may be sprayed to an appreciable thickness over a thin silver coating of 0.001 inch or less and still maintain low contact resistance. Copper is preferred as a silver overcoating because of its conductivity, ductility and hardness.

Silver was also deposited on massive lead dioxide by reduction from a solution. A silver salt solution and a reducing solution were fed through a specially designed spray gun, the two sprays mixing just before hitting the object to be silvered. It was found necessary to first activate the lead

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dioxide surface with a solution of stannous chloride before silver coating. This silver to lead dioxide potential drop was 0.0004 volt at one ampere.

An attempt to plate silver on lead dioxide from a silver cyanide bath was not successful. The deposit formed was not conducting and appeared to be lead monoxide. Copper was electroplated on lead dioxide from an acid sulfate bath, but from a copper cyanide bath, the result was similar to that from a silver cyanide bath.

A current contact area was formed on the upper 4-3/4 inches of lead dioxide electrode #219 (see Table II) by spraying on silver and copper with the "Metco" wire spray gun. A coating of silver probably not more than 0.001 inch thick was first formed on the lead dioxide. Four #10 gauge copper wires were then fastened vertically to each face of the electrode in the silver sprayed area by means of cross tying #14 gauge copper wires. The tops of the #10 wires extending above the silver coated area were soldered to 1/4 inch thick brass plates which were then covered with masking tape. The silver coated area was heavily spray coated with copper to a thickness of about 1/8 inch to bind the copper wire assembly to the electrode.

Measurement of potential drop between the sprayed copper and lead dioxide at one ampere gave a value below 0.0001 volt. This electrode was successfully operated at 100 amperes in the chlorate-perchlorate cell as described in Section A2c of this report, and illustrated in Figure 8. Another electrode with a similarly formed current contact area is shown in Figure 9.

Current contacts were similarly formed on electrodes #221 to #230 (see Table II) by the Colmonoy Sprayweld Process. However, on these rod electrodes, a spiral copper wire current lead could not be bound to the electrode by the copper spray. Soft soldering of the copper wire lead to the copper spray coating proved satisfactory.

All of the above metal spraying was done on the as-plated surface of the lead dioxide. Such a surface was more or less crystalline and similar to the surface of fine emery cloth. This provided many points for binding the metal coatings to the lead dioxide. The metal spray coatings tended to peel badly from the surface of flat electrodes which had been machine ground to form parallel plane faces. Even after the ground surface had been grit blasted to provide some roughening, metal coatings thicker than a few thousandths inch cracked and peeled.

g. Other Forms of Lead Dioxide Electrodes

Lead storage battery grids were tested as anodes in the chlorate-perchlorate cell. The electrode consisted of an anodized lead battery sheet, that is, compacted lead dioxide in a lead grid which was obtained as a sample from

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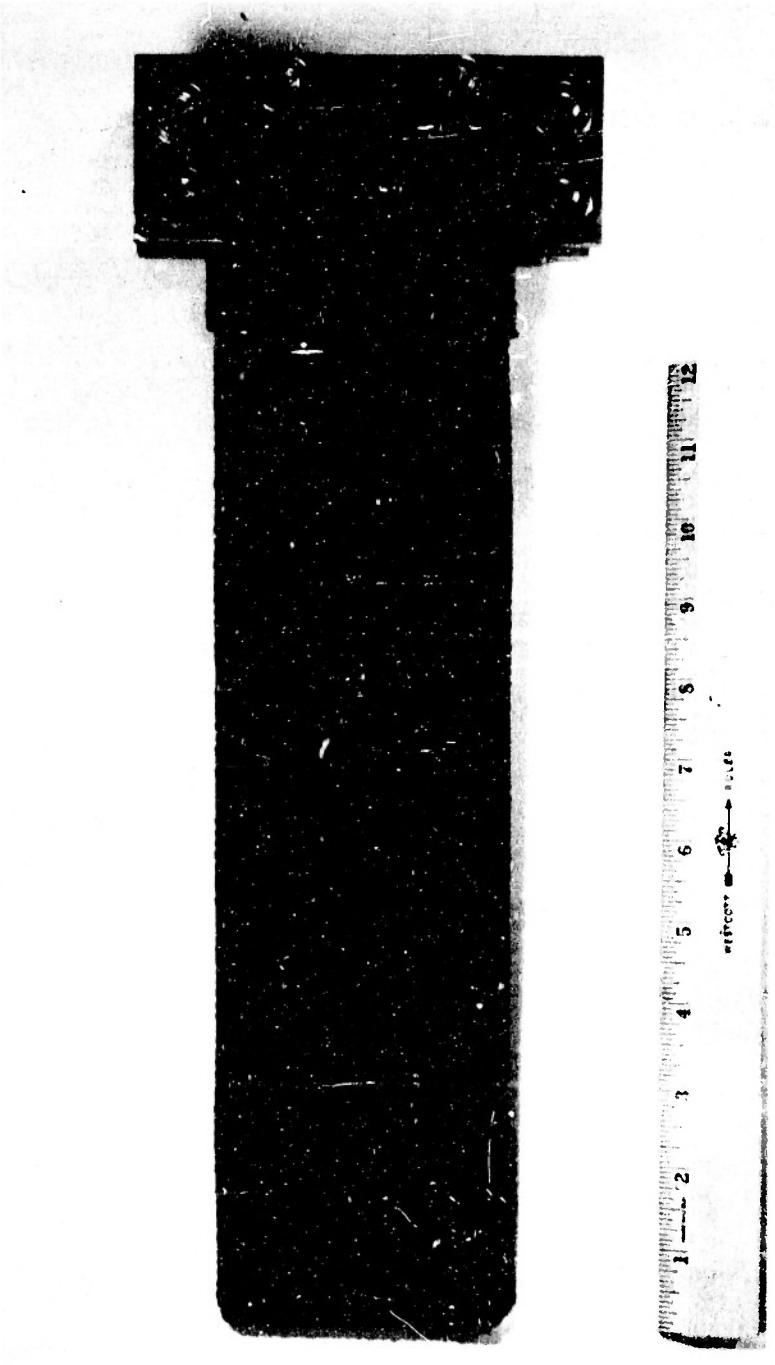
FIGURE 9

MASSIVE LEAD DIOXIDE ELECTRODE WITH METAL SPRAYED CONTACT CURRENT



NOTE: In operation, the cable lugs would be fastened to each of the two brass plates shown clamped to the copper over silver sprayed current contact.

Electric Storage Battery Co., Philadelphia, Pennsylvania. In operation, the anode portion above the electrolyte level heated to about 80°C. for the first two to three hours and then ran cool. The electrolyte was light brown after 24 hours. The anode failed at 30 hours due to complete erosion of the supporting lead grid at the solution-air interface, and the lead grid throughout the immersed portion of the anode was seriously eroded. A current efficiency of 39 percent was obtained.

In an attempt to produce a lead dioxide coating by means other than normal electroplating, lead tubing was anodized to form a lead dioxide film. The lead tube was first degreased in 5 percent sodium hydroxide solution, pickled in 15 percent nitric acid, and then successively anodized at 25 amps./ft.^{2} and 25°C. in a 30 g./l. sodium cyanide solution for 6 minutes, and a 75 g./l. sodium carbonate solution for one hour. A white coating with brown spots was formed in the cyanide bath. This was subsequently converted to a velvety brown coating in the carbonate bath. On testing in the chlorate-perchlorate cell at 0.1 amp/cm^2 more than half of the coating came loose and was dispersed in the cell within five minutes. The lead tube was rapidly attacked, and fuzzy lead was plated on the cathode. The electrolyte turned milky, and its pH rose from 3.3 to 10. The same results were obtained with an initially alkaline electrolyte.

3. Physical Properties of Lead Dioxide

a. Electrical Conductivity of Lead Dioxide

Upton B. Thomas of the Bell Telephone Laboratories (3) measured the electrical conductivity of dense samples of lead dioxide prepared by the electrolysis of lead perchlorate and lead sulfamate. The specific resistance of these dense samples was of the order of 200 x 10^{-6} ohm-cm. The specific resistance of porous samples prepared from storage battery oxides was 7400 x 10^{-6} and porous samples prepared from pressed powder was 14,200 x 10^{-6} ohm-cm. (see Table XI).

Thomas made electrical contacts to the lead dioxide sample by one of three ways:

(1) copper wires were cemented to the PbO_2 with conducting cement

(2) thin strips of silver foil were pressed directly against the specimen; or

(3) against areas on its surface, onto which a thin layer of gold has been evaporated.

W.H. Palmaer (4) measured the electrical properties of lead dioxide made by electrolysis of a dilute lead nitrate solution.

He found the specific resistance of lead dioxide to be 92 x 10^{-6} to 97 x 10^{-6} ohm-cm. with a positive temperature coefficient of 0.06 percent per degree in the range of 22-84°C.

At Pennsalt, the specific resistance of a piece of massive lead dioxide (5.7 cm. x 2.5 cm. x 0.7 cm.) plated from an acid lead nitrate bath was measured. The original nodular plate was cut with a diamond saw to obtain smooth surfaces. Electrical contact was made at the ends of the dense lead dioxide by first wrapping on copper foil and then tightly wrapping thin copper wire over the foil. This was pressed firmly against the lead dioxide by screw-type hose clamps. Current was passed through the lead dioxide (4 and 8.6 amperes) and the voltage drop across a 2.54 cm. length of lead dioxide was measured by pressing probes leading from a Rubicon potentiometer firmly against the lead dioxide. The copper-lead dioxide contacts were not satisfactory, as evidenced by the fact that the whole assembly became hot. The specific resistivity according to these measurements was from 40 to 50 x 10^{-6} ohm-cm.

Thus lead dioxide has characteristics which more nearly approach those of metals than those of semi-conductors. Its conductivity is much higher than that of most semi-conductors, and decreases with temperature. Dense lead dioxide is more conducting than graphite (800 x 10^{-6} ohm.-cm.) and its specific resistance is about equal to that of the poorly conducting metals such as mercury and bismuth.

b. Specific Gravity

W. H. Palmaer (4) measured the specific gravity of lead dioxide electrolyzed from dilute lead nitrate solution. Its specific gravity at 20°C. was 9.36.

In the present study a massive piece of lead dioxide electrolyzed from the acid lead nitrate bath (Formula LN-2) had a specific gravity of 9.32 at 24°C.

c. Hardness

W. H. Palmaer (4) found that the hardness of electroplated lead dioxide was between 5 and 6 on the Moh scale.

In the present study, the massive lead dioxide plates have been hard (not measured) causing difficulty in machining off nodules formed on thick plates. Such samples given to Carborundum Company were found by them to machine easily in the following manner (6):

(1) Grinding with Carborundum Brand - A 36-06-V30 wheel, 8" diameter x 1" wide, and

(2) Cutting with a metal bonded diamond wheel - No. 18005, 8" diameter x 0.045" wide (60 grit, 25 concentration).

4. Safety Precautions in Handling Lead Compounds

Lead poisoning (7) is one of the oldest and best known of all occupational diseases and it may be found wherever lead or lead compounds are used. Inorganic lead compounds may be absorbed either by inhalation or by ingestion. There is said to be no evidence that inorganic lead compounds can be absorbed through healthy unbroken skin in quantities sufficient to produce lead intoxication. However, lead compounds on the hands frequently will result in the ingestion of these substances. Both soluble and insoluble compounds can produce symptoms of lead intoxication. Therefore, whenever lead or lead compounds are used, great care must be used to prevent lead intoxication in the workers. Good housekeeping, rubber gloves, dust masks, and sound sanitary habits are required if the lead hazard is to be avoided.

With careful control of working conditions and procedures and close medical observation of the workers, there is no danger of serious lead poisoning.

In the electroforming of massive lead dioxide electrodes there is frequent possibility of human contact with the lead nitrate or other soluble lead salt solution of the plating bath. Also, in the replenishment of the plating bath with lead monoxide, or litharge, as it is commonly known, this finely divided powder is transferred by scoop from the original container to weighing containers to the replenishing tank of the plating bath. In these handling operations there is a tendency for some lead oxide dust to be dispersed into the atmosphere, and also to adhere to all objects which touch it.

The finished lead dioxide electrode, itself being hard and compact, can be considered to be inert so far as the danger of lead poisoning is concerned. In cases where the lead dioxide electrode is to be surface ground or cut, there will be a lead oxide dust dispersed into the atmosphere just as in the handling of powdered litharge.

5. Review of Japanese Literature on Massive Lead Dioxide

An apparently sustained effort on the preparation of lead dioxide electrodes and their application to various electrolytic oxidation processes including the production of sodium perchlorate has been carried on by various Japanese investigators at the Tokyo Institute of Technology for the past 20 years. English translations of three papers and a Japanese patent on this work have recently been received.

The first paper by Kato and Keiruni (8) was published in 1934 and is titled "A New Process for the Preparation of Lead Peroxide Anodes". A 30 percent solution of lead nitrate containing a hydrophil such as gelatin was used for a lead dioxide plating bath, and it was recommended that the bath be operated at 80°C. and an anode current density of 100 amps./dm.^{2}, (929 amps./ft.^{2}). The lead dioxide which was deposited on graphite and nickel was said to be very fine with no pores and was made in flat plates up to 20 by 14 cms. In a discussion of oxygen overvoltage, it was stated

that the value for lead dioxide was somewhat higher than platinum and thus it could be used as anode in the electrolysis of sodium chlorate to perchlorate. A 50 percent sodium chlorate solution containing 5 percent sodium dichromate was used as electrolyte. The bath temperature was maintained at 5°C. and the current density at 12 amps./dm.^{2} (111 amps./ft.^{2}), under which conditions the cell voltage was 4.9. A current efficiency of 58 percent was attained with the lead dioxide anode as compared to 81 percent with platinum at the same current density. However, when the current density of the platinum was increased to its normal value of 30 amps./dm.^{2} the same amount of perchlorate was produced in both cases by equal amounts of power.

Kato and co-workers (9) published a paper in 1941 titled "Outline of Semi-industrial Research for the Electrolytic Preparation of Sodium Perchlorate with New Metal-like Lead Peroxide Anodes". They reported the oxygen overvoltage of lead dioxide to be 0.15 volts lower than that of polished platinum in 1-N KOH at 30°C. and a current density of 10-20 amps./dm.^{2} (92.9-185.8 amps./ft.^{2}). Their plating bath composition and operating conditions were very similar to those described above, except that a lower current density, 15-20 amps./dm.^{2} (139-186 amps./ft.^{2}), was used, the cathode was graphite or a rotating copper rod, and the lead dioxide was plated to a thickness of 7 mm. on the inside of a nickel cylinder. This plated cylinder with the provision of a suitable bottom then served as the chlorate-perchlorate cell container. On electrolysis of a 40 percent sodium chlorate solution at an anode current density of 17 amps./dm.^{2} (158 amps./ft.^{2}), and a cell temperature of 26°C., a current efficiency of 44 percent was obtained with an 86 percent conversion of chlorate to perchlorate. A sudden drop in current efficiency at 85 percent conversion was explained as being caused by the reduction of perchlorate at the cathode. The current efficiency was increased to 57 percent with the reaction carried to 99 percent completion when a small piece of platinum (1-2% of area of PbO_2) was placed in the cell connected in parallel with the lead dioxide. The increased current efficiency was attributed to deposition of dissolved platinum on the cathode, thereby lowering the hydrogen overvoltage of the cathode and preventing cathodic reduction of perchlorate.

Direct electrolytic production of sodium perchlorate from sodium chloride in a single electrolysis was also carried out, using the above lead dioxide anode with an overall current efficiency of 49 percent.

During extended electrolysis with the anode consisting of lead dioxide on nickel, the nickel base was oxidized, causing contact resistance between the lead dioxide and nickel to increase, and thus the voltage for electrolysis to rise. In addition, the electrolyte seeped through pinholes in the lead dioxide and dissolved the nickel base, causing electrode failure. It was found possible to separate the lead dioxide from the nickel base by cooling, and obtaining a long lived electrode, taking advantage of the greater coefficient of thermal expansion of lead dioxide. Electrical connection was made at the top end of this electrode to a part of the nickel base that had not been removed.

Sugino (10) published an abstract in 1950 of twelve previously published papers on "Preparation, Properties, and Application of the Lead Peroxide Electrode Manufactured by a New Method". His

lead dioxide plating bath composition and operating conditions were very similar to those described in the above two papers. A lower anode current density of 6.96 amps./dm.^{2} (64.6 amps./ft.^{2}) was used, no hydrophil addition agent was added to the plating bath, and the lead dioxide could be plated on the inner surface of an "iron" cylinder by using a neutral lead nitrate solution. During electrolysis, the pH and concentration of lead ion were maintained constant by continuously circulating the electrolyte through an external train system consisting of a holding tank, a neutralizing tank in which $Pb(OH)_2$ was kept in suspension by agitation, a filtering bed, and a reheating tank from which the replenished and neutralized electrolyte was returned to the cell. The "iron" cylinder was cut away from the inner electrodeposited lead dioxide cylinder, and the lead dioxide was then cut lengthwise into sixteen rectangular strips 300 mm. x 45 mm. x 8-10 mm. thick. Current contact was made to the lead dioxide by first wrapping silver foil around the upper end, and then tightly clamping an aluminum or brass strip over the silver, the anode lead then being fastened to this clamp.

In an alternate method, the lead dioxide was deposited from neutral lead nitrate at 27-31°C. on the outer surface of a rotating rod which was covered with a paraffin-graphite mixture. A hollow cylinder of lead dioxide was then obtained by melting the paraffin and sliding out the rod. The plating bath for this use was modified by the addition of 10-30 g./l. $Cu(NO_3)_2$ and 60-80 g./l. $NaClO_4$.

The lead dioxide anode was reported to be a good conductor, carrying above 20 amps./dm.^{2} (186 amps./ft.^{2}), and almost perfectly insoluble. On electrolysis of sodium chlorate solution using this lead dioxide anode and 18-8 stainless steel cathode at 20 amps./dm^2 (186 amps./ft.^{2}) and 30°C., a current efficiency of 41% was obtained on a 99.9 percent conversion of chlorate to perchlorate. The addition of 2 g./l. of sodium fluoride was found to increase the current efficiency to 82 percent over the same concentration range. Direct electrolytic production of sodium perchlorate from sodium chloride was similarly carried out, except that during the initial stage of electrolysis from Cl^- to ClO_3^- the cell temperature was maintained at 60-65°C. and a small amount of hydrochloric acid was added from time to time to maintain the electrolyte slightly acidic. When the chlorate formation was almost complete, 2 g./l. sodium fluoride was added to increase the chlorate to perchlorate current efficiency. An overall current efficiency of about 60 percent was obtained. This method for direct electrolytic production of sodium perchlorate is covered by Sugino in a Japanese patent (11) issued in 1946. Potassium chlorate was electrolytically formed from potassium chloride at a current efficiency of 81 percent.

The oxygen overvoltage of the lead dioxide anode was measured in 1N sulfuric acid at 30°C. at various current densities and compared with that of smooth platinum. The values for lead dioxide were found to be somewhat lower than for platinum, for example, 0.16 volts lower at 1 amp./dm.^{2} (9.3 amps/ft.^{2}). On addition of various amounts of hydrofluoric acid, it was found that the overvoltage of lead dioxide increased with the logarithm of the concentration of hydrofluoric acid.

The procedures described in the above papers were generally confirmed by the work of the present ONR project. However, the use of the natural hydrophil gelatin, as addition agent in the plating bath resulted in a lead dioxide of low fracturing strength. Therefore, a synthetic surface-active agent was substituted, permitting increased effectiveness in producing a fine-grained lead dioxide deposit with maximum strength and density. Also, the Japanese did not reveal the use of a lead dioxide base material such as tantalum which would be completely inert during anodic electrolysis of sodium chlorate solution. The problem of current contact to the lead dioxide was recognized, but the Japanese technique, consisting of a metal clamp over silver foil wrapped on the lead dioxide is only partially satisfactory. Reported cell current efficiencies were comparable with those obtained during the present project. However, the reported beneficial effect of sodium fluoride addition in raising the current efficiency was not completely confirmed.

B. Miscellaneous Anode Materials - Screening Tests

1. Summary of Previous Work Done Under 1951 Project NR 352-263/2-19-51 and 1952 Project NR 352-304/2-1/52

Tantalum carbide containing 17% platinum by weight obtained from the Carboloy Department of General Electric Company gave favorable results with repeated tests. Anode loss rates varied from 1×10^{-5} to 20×10^{-5} grams per ampere hour, and current efficiencies as shown by electrolyte analysis have been as high as 70%.

Plattnerite, a rare, naturally occurring massive lead dioxide, operated smoothly as anode in the chlorate-perchlorate cell at a low voltage without shattering and with very slight erosion.

Magnetite anodes showed slight erosion but produced sodium perchlorate at a current efficiency of only about 4 to 5%.

Platinum plated tantalum sheet performed entirely satisfactorily as an anode material.

The mineral ilmenite from Ward's Natural Science establishment behaved well in screening tests conducted in 1951. No further work has been done on this material since that time.

All other materials which are listed in detail in the reports for 1951 and 1952 proved to be unsatisfactory.

2. Work Done in 1953 and 1954

Of the miscellaneous anode materials thus far examined in screening tests, the following appear promising enough to justify further investigation:-

a. Manganite ($Mn_2O_3 \cdot H_2O$),
b. a tin oxide block, sample B53 (Pittsburgh Plate Glass Co.)
c. 95% platinum and 5% palladium, and
d. 90% platinum and 10% palladium.

All other materials which are listed in detail in the following paragraphs proved to be unsatisfactory.

Samples of bearing materials (carbon impregnated with various metals) from the Carbone Corporation, Boonton, N.J. were tested in the chlorate-perchlorate cell. These samples were RSS Copper, RS Copper, RSS Babbitt, RS Babbitt and RS Silver, with the RSS material being somewhat harder and stronger than the RS material. The specific resistance of these compositions was of the same order of magnitude as that of graphite, but when tested as anodes, all eroded rapidly with the RS Silver composition showing the least, but still appreciable, attack (See Table XII).

Electrical Conductivity Ratings of Some Minerals

Several thousand specimens available in the University of Pennsylvania's collection were screened for their potential value as electrical conductors and eighty-three were selected for cell testing. Voltage drops were made across a clean portion of each mineral. The resulting readings were compared to similar readings made on well-known materials of varying degrees of conductivity. The results were grouped into the following categories: those minerals whose conductivity was similar to that of graphite were rated as excellent; those similar to carbon were rated good; those similar to pyrolusite were rated poor; while those much below this were rated very poor; and those showing no passage of current were classed as non-conductors. It was observed that the conductivity varied greatly in different specimens of the same mineral species. The results are listed in Table XIII. The naturally occurring metals and metal alloys which are known to be good conductors are not listed in this table.

In order to round out our survey of useful materials for anodes in the perchlorate cell, the following minerals were selected from Table XIII for testing on the basis of their relatively high conductivity: cassiterite from England, cassiterite from South Dakota, psilomelane (orthorhombic), psilomelane (massive), ilmenite, hematite, pyrolusite and zincite. These minerals were purchased from Wards Natural Science Establishment. All failed because of rapid erosion, high contact resistance or polarization as may be seen from Table XIV. Also poor current distribution within the sample was observed because the mineral samples were non-homogeneous.

A sample of silicon ferrite from Horizons, Inc. eroded rapidly when tested as an anode in the chlorate-perchlorate cell, as did a sample of impervious graphite from Falls Industries, Solon, Ohio. However, a sample labelled pyrolusite (MnO_2 + 2% H_2O) obtained from the Pennsylvania State University showed very little erosion. This sample later proved to be manganite ($Mn_2O_3 \cdot H_2O$) by X-ray analysis.

Natural graphite (Rhombohedral, Colombo Mines, Island of Ceylon) from Ward's Natural Science Establishment eroded very rapidly.

A nickel-ferrite boule from the Linde Air Products Company, which was previously reported as a poor conductor (page 25, Second Quarterly Research Report for 1952), was found to have a non-conductive outer layer. After grinding this outer layer off, the inner layers were found to be conductive enough to be tested as an anode in the chlorate-perchlorate cell. There was no appreciable erosion, but conversion of chlorate to perchlorate was very low.

A 24 carat gold rod was attacked as evidenced by a weight loss, the formation of an orange precipitate in the electrolyte and also the formation of a rust-colored film on that portion of the gold rod immersed in the electrolyte.

The testing of silver sheet as anode in the mildly alkaline electrolyte (pH = 8.5) in the chlorate-perchlorate cell resulted in rapid and uneven etching of the silver and the formation of a dark gray smut over the anode surface. A high rate of erosion also resulted when the silver was first anodically electrolyzed in 15% sodium hydroxide solution to form a black deposit.

A sample of electrolytic manganese eroded rapidly when tested in the chlorate-perchlorate cell. Some explosions were observed in the cell.

Details of the testing of the above materials are given in Table XV.

Polished plate glass samples with a conductive film on one side fabricated by Pittsburgh Plate Glass Company failed rapidly. They operated at low current and high voltage with either the conductive film coming off as a cloud, the plate glass cracking at the electrolyte level, or the current lead melting off because of the heat generated.

Tin oxide blocks, also furnished by Pittsburgh Plate Glass Company were more promising, showing: for Sample A123, slight amount of erosion and about 15% current efficiency; Sample B92, contact difficulties were so great that current efficiency could not be obtained; Sample B8, no erosion and about 17% current efficiency; and Sample B53, no appreciable erosion and about 50% current efficiency. Further samples of the Type B53 should be tested (see Table XVI).

Samples of conducting glasses and refractories from the Corning Glass Works either eroded or operated at a very high cell voltage, (see Table XVII).

Pressed and fired mixtures of lead dioxide were fabricated for testing as anode materials. Powdered mixtures of C.P. lead dioxide and minus 250 mesh magnetite with and without a binder (50% potassium hydroxide and 38° Baume sodium silicate solution) were pressed at 15,000 pounds per square inch and then fired in air or oxygen at 300°C. Some of these specimens were hard and showed good conductivity. The most promising of these samples as shown by conductivity tests and mechanical disintegration tests in sodium chlorate solutions were chosen for perchlorate cell anodes. All showed considerable mechanical disintegration. (See Table XVIII).

Small bars of lead dioxide with small amounts of lead added as a binder received from Julius J. Harwood, Metallurgy Branch, Department of the Navy, ONR, Washington 25, D.C. (Letter File No. ONR:423:JJH:ehc, 21 April 1953) were somewhat fragile and were broken when received. However, the largest piece was tested as an anode in the chlorate-perchlorate cell and, although some erosion was present, this sample eroded the least of the pressed PbO_2 samples thus far tested. Electrical contact was made by casting lead over nickel wire wrapped around the top portion.

Samples of Borolite III A representing three different chromium boride to binder ratios and manufactured by the Electro Metal Corporation were received through Dr. J.J. Harwood of the Office of Naval Research. All samples eroded rapidly and turned the electrolyte a dark brown color in five to six hours (see Table XIX).

PLATINUM Group Metals and Their Alloys

The only members of the platinum group metals that could help solve the problem of this research without introducing more serious problems are ruthenium and palladium. The literature implies that these metals do not work satisfactorily as anodes in the perchlorate cell (12). However, there is no clear information on the behavior of alloys of these metals in the electrolytic preparation of perchlorates. It is possible to mix platinum and palladium in all proportions to form workable alloys. However, ruthenium can be alloyed with platinum or palladium only to about 12% if an alloy with usable physical properties is to result.

Several such alloys were obtained from Baker and Co., Inc., 113 Astor Street, Newark (5), N.J.

In the system platinum-palladium as shown in Table XX, samples of 95% platinum and 5% palladium, and 90% platinum and 10% palladium showed practically no erosion loss as was also the case with 100% platinum. However, there was a definite erosion loss with a sample of 80% platinum and 20% palladium and this erosion loss increased as the palladium content of the alloy increased until with 100% palladium, the erosion loss was 5.2 milligrams per ampere hour. A few current efficiency studies indicate that the current efficiency falls off as the palladium content of the alloy increases.

Large scale tests over long periods of time would be necessary to accurately determine erosion rates and current efficiencies of platinum-palladium alloys high in platinum (80 to 95% platinum). Thus, tests would show whether there would be any advantage of using these high platinum-palladium alloys in place of pure platinum in commercial perchlorate cells.

In the system platinum-ruthenium (Table XXI), an anode of 88% platinum and 12% ruthenium eroded very slightly, showing an erosion loss of from 0.002 to 0.005 milligrams per ampere-hour, when the cell electrolyte was held at about 10°C. When the cell electrolyte was kept at about 45°C., the erosion loss was somewhat greater, being about 0.03 milligrams per ampere-hour. A sample of pure ruthenium, when tested under similar conditions, showed an erosion loss of about 27 milligrams per ampere-hour with an orange-yellow precipitate forming in the electrolyte. The ruthenium sample became black.

A sample of 88% palladium and 12% ruthenium (Table XXII), eroded with a loss of 4.0 milligrams per ampere-hour with a brown precipitate forming in the electrolyte. The sample was colored reddish-brown at the conclusion of the test.

Electroplated Manganese Dioxide

The plating bath of Storey, Steinoff and Hoff (13), an acid solution of manganese sulfate at a concentration of 150 g./l., was first used in attempts to plate manganese dioxide. At anode current densities of 0.5 to 20 amp./ft.^{2}, flash coatings of manganese dioxide as formed on the anode repeatedly flaked loose. Cell voltage rose sharply during plating. Conductivity of the manganese dioxide was poor.

From a manganese nitrate bath at a concentration of 179 g./l. and an anode current density of 10-20 amp./ft.^{2}, manganese dioxide formed on tantalum rod in thin, repeated layers each of which partially flaked loose before formation of succeeding layers. The deposit was built up to a thickness of about 3/64 inch, and had a lustrous, black surface marked with many closely spaced gas holes. Also, the manganese dioxide was weak and easily fractured by finger pressure. No further work with manganese dioxide was planned.

C. Silicon-Silicon Carbide Mixtures as Anodes

1. Method of Preparation

The anode materials submitted to Pennsalt for testing by the Research and Development Division of the Carborundum Company consisted primarily of compositions of silicon and silicon carbide. These compositions have been given the trademark name "Durhy" by the Carborundum Company. Two general methods of forming these materials were followed:

(a) Cold pressing a mixture of silicon and silicon carbide followed by sintering in a protective atmosphere. Variations in these compositions were made by changing the silicon-silicon carbide ratio and also by combining addition agents in the mix before pressing. This product is designated Durhy #1.

(b) Pressed silicon carbide with a temporary binder is recrystallized by the passage of a high electric current through the body with the temporary binder passing off and a new crystal structure of silicon carbide being formed. This recrystallized silicon carbide is impregnated with silicon by placing the body in molten silicon, resulting in the composition known as Durhy #1.

(c) Impregnation of a carbonaceous body with silicon metal by placing the body into a bath of superheated molten silicon metal. The silicon metal impregnated the carbonaceous body and reacted with it to form silicon carbide, resulting in a body whose components are silicon carbide, silicon and some free carbon. This material is called Durhy #2. Variations in compositions in the Durhy material were made by additives to the silicon metal and by forming carbon bodies from different materials by carbonization.

Some anodes were treated thermally, chemically, and physically to produce variations in surface and internal structures (14).

2. Summary of Previous Work Done Under 1951 Project NR 352-263/2-19-51 and 1952 Project NR 352-304/2-1-52.

In 1951 screening tests and the operation of a 10 ampere cell showed that Durhy #2 (silicon-silicon carbide mixtures) produced perchlorate with little or no normal surface erosion; however this material was always seriously damaged by cracking and shattering upon electrolysis. This effect was particularly noticeable at the top level of the electrolyte. With Durhy #1, polarization of the anode rapidly occurred.

In 1952, 52 samples representing 24 different kinds of materials were obtained from Carborundum Company under the Pennsalt-Carborundum contract agreement. After testing as anodes in the chlorate-perchlorate cell, most of these samples again showed the spalling or polarization characteristic found before, and a few samples exhibited rapid erosion. However, an extruded Durhy #2 composition quenched in molten lead, and a 90% silicon-10% silicon carbide composition showed sufficient promise to be investigated further

(See Work Done in 1953). Up to the end of 1952 no satisfactory silicon-silicon carbide composition for use as anode in the chlorate-perchlorate cell had been found.

3. Work Done in 1953 and 1954

During the period from January 1,1953 to January 31, 1954, about 310 samples representing about 116 different kinds of materials were received from the Carborundum Company and tested in a small beaker-type chlorate-perchlorate cell.

In summary, it was found that these materials showed considerable improvement over those tested previously in that certain types polarized far less rapidly than before, and others operated at low cell voltage, making perchlorate for a considerable length of time before exploding or spalling. The promising materials found were: calcined. untempered Masonite; calcined, tempered Masonite, calcined Homasote; and calcined Compreg; all impregnated with silicon.
The Durhy #2 quenched in molten lead has been eliminated from further consideration (See Work Done in 1952), since the residual lead content was shown to account for its early quiet operation. After the lead is eroded away, the quenched electrodes behave like unquenched Durhy #2. No further work is contemplated with these lead quenched Durhy #2 compositions because of their exploding and spalling characteristic after their lead content has been removed.

To date no entirely satisfactory silicon-silicon carbide composition has been found for use as anode material in the chlorate-perchlorate cell.

The detailed tests of silicon-silicon carbide materials (*) for 1952 and 1953 are shown in the following tables according to the different categories given by the Carborundum Company:

No.	Category
1.	Cold pressed and sintered Si-SiC series
2.	Silicon alloy impregnation
3.	Variations in carbon bases
4.	Heating and quenching treatments
5.	Surface treatments, chemical and physical, and atmospheres
6.	Impregnants (other than silicon) and coatings
7.	Cast silicon
8.	Variations in physical dimensions
9.	Coated graphite or carbon
10.	Miscellaneous

These anode materials were tested in small beaker type cells (400 ml) each equipped with a glass cooling coil. By circulating tap water through the glass cooling coil, the sodium chlorate electrolyte (600g/l) was kept at a temperature of about 12°C. Two stainless steel cathodes were used, being held in place by a Plexiglas cell lid. Whenever possible, four to six cells were operated in series.

(*) Each sample was numbered consecutively with the category number as a prefix.

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Category No. 1 - Cold Pressed and Sintered Si-Si C Series

The silicon-silicon carbide compositions fired in an atmosphere of carbon monoxide either gave very little erosion or no erosion at all and no spalling. A few very small explosions were observed with some samples. Similar compositions fired in a helium atmosphere behaved like the carbon monoxide treated compositions with very little erosion and no explosions. The cell voltage seemed to increase about three times faster with the helium treated compositions than with the carbon monoxide treated ones (See Figure 8). Thus it appears that the carbon monoxide has a beneficial effect.

However, the high specific resistivity and polarization characteristic of these materials eliminates them from consideration.

A number of addition agents were tried in the silicon-silicon carbide compositions fired in an atmosphere of carbon monoxide. These addition agents included calcium fluoride, magnetite (Fe_3O_4), lead and tantalum carbide. These materials showed either slight erosion or no noticeable erosion, but all had high specific resistivity and operated at high cell voltage after a short period of operation.

The beta silicon carbide, silicon and carbon mixture (No. 1-33), the silicon, silicon carbide and manganese dioxide mixture (No. 1-31), as well as the silicon, silicon carbide and $FeO \cdot TiO_2$ mixtures (No. 1-40 and 1-41), eroded very rapidly (Table XXIII).

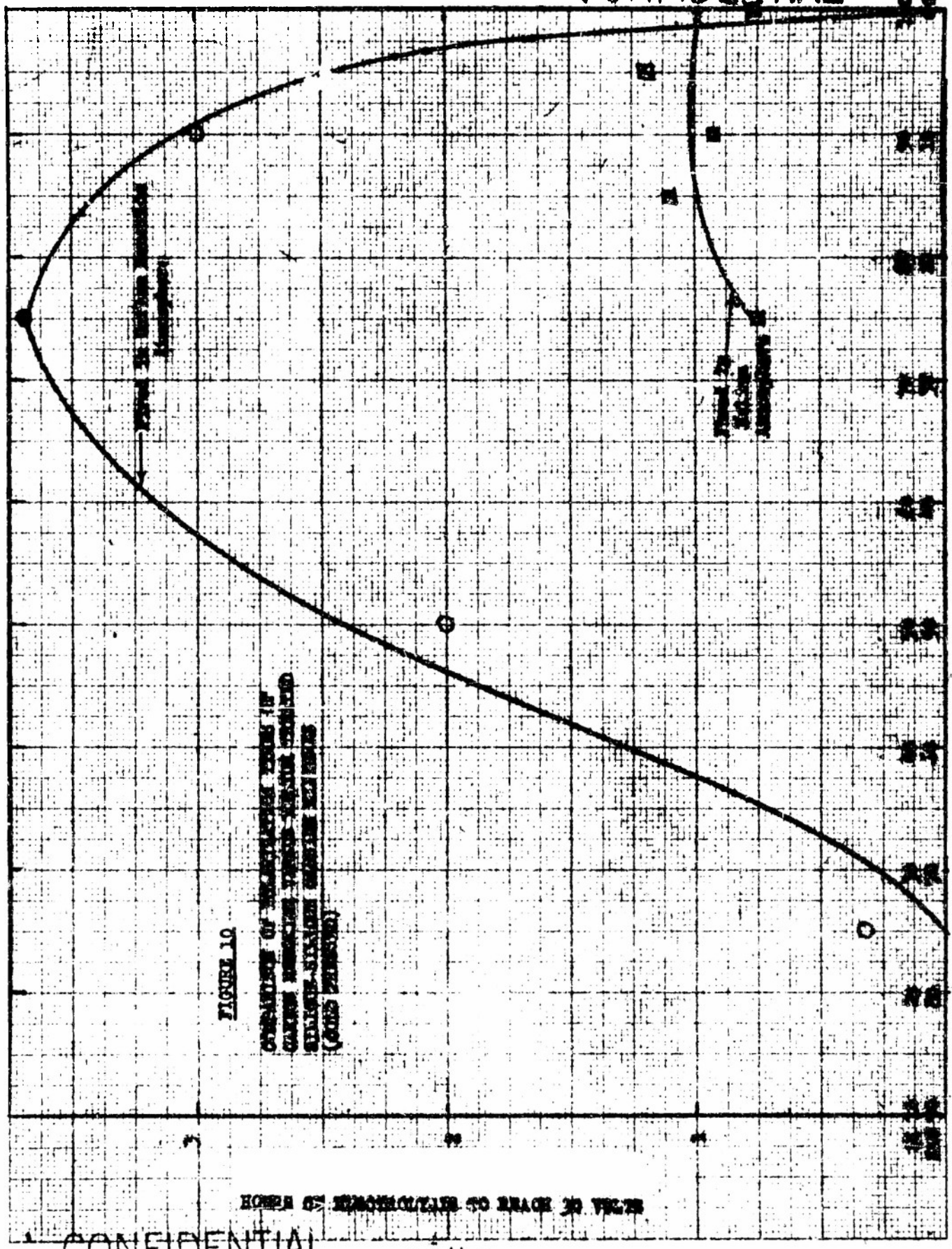

FIGURE 10

Category No. 2 - Silicon Alloy Impregnation

All the anode samples in this group exploded, causing early and complete failure of the anode except the calcined extruded material impregnated with Electromet silicon-titanium alloy (No. 2-18), and with Electromet 35-40% zirconium alloy (No. 2-19), both of which eroded in half at electrolyte level after 19-24 hrs. of operation. (See Table XXIV).

Category No. 3 - Variations in Carbon Bases

Of this group, samples of calcined untempered Masonite board, impregnated with silicon (No. 3-7 and No. 3-24), behaved well, operating with no explosions and no or slight erosion. Current efficiencies varied from 18 to 30%. There was a gradual increase in cell voltage. After polarization, soaking of the anode sample in 50% aqueous HF and then rinsing well, resulted in a short period of operation at low cell voltage. The original high cell voltage returned after several hours of operation.

Calcined tempered Masonite, impregnated with silicon (No. 3-25) operated at better current efficiency but with some erosion.

The following calcined materials impregnated with silicon behaved as follows: wood doweling, no noticeable erosion, rapid polarization; bamboo, erosion with one sample finally breaking off at electrolyte level, about 60% current efficiency; Homasote, slow polarization, a few explosions blew off some particles of anode material; manila rope, slow polarization, failed by breaking off at electrolyte level; sash cord, slow polarization, erosion; mailing tube, erosion observed; hard wood charcoal, explosions and heavy erosion noted and walnut shells, some erosion with slow polarization.

With the calcined Compreg samples, impregnated with silicon, one sample (No. 3-19) showed no appreciable erosion but cracked at electrolyte level while the other sample (No. 3-26) showed some erosion.

All of the porous carbon and graphite samples impregnated with silicon eroded rapidly with no cell explosions.

The Durhy material made by siliconizing a carbon body formed by extruding a mixture of wheat flour and carbon powder showed severe spalling. Also the Durhy material made by siliconizing a carbon body formed by casting, polarized and showed slight spalling.

An extensive study was made of the calcined masonite materials and other calcined materials impregnated with silicon (Samples 3-27 through 3-32). All these samples showed erosion but operated without exploding. Current efficiencies varied from 75 to 35% for a short period of electrolysis of 20 to 30 ampere-hours; but when tested for longer periods (about 60 to 70 ampere-hours), current efficiencies were much lower, ranging from 10 to 20%. (See Table XXV).

Category No. 4 - Heating and Quenching Treatments

As may be seen from Table XXVI, all the samples of Durhy #2 given heating or quenching treatments operated with explosions, either causing chunks of anode material to fall off or causing the anode sample to blow apart, except the extruded Durhy #2 quenched in molten lead from 1350°C. (No. 4-6).

This lead quenched Durhy #2 behaved favorably, operating at low cell voltage for 14.5 hours with some erosion of the lead from the sample as evidenced by the muddy color of the electrolyte. At the end of this period there was an explosion, blowing off one large piece of anode. When the lead was removed from the sample by soaking in 35% nitric acid for 3 days, it behaved like Durhy #2 with frequent explosions. Thus it seems that the lead content of the original sample was responsible for the favorable behavior of this lead quenched Durhy #2 (see Table XXVI).

Category No. 5 - Surface Treatments, Chemical and Physical, and Atmospheres

Durhy #2 samples treated by an aqueous HF-HNO_3 mixture, by an aqueous HF solution and by a caustic solution showed rapid surface erosion and spalling. No explosions were observed.

Globar heating sections, treated by aqueous HF and by nitric acid eroded appreciably particularly at the electrolyte level with the samples finally breaking off at this point.

Extruded Durhy #2 tumbled in SiC grain and also in Al_2O_3 grain operated with severe spalling and numerous explosions in the cell.

Decarbonized Durhy #2 polarized as did a sample of Durhy surface-smoothed with a diamond wheel. The latter sample also showed slight spalling (see Table XXVII).

Category No. 6 - Impregnants (other than silicon) and Coatings

The Globar heating sections impregnated with furfural (No. 6-1), with linseed oil (No. 6-3), with silicone water repellant (No. 6-5) and with paraffin (No. 6-7) operated at too high a cell voltage to be considered practical.

The Durhy #2 samples impregnated with linseed oil (No. 6-4), with silicone water repellant (No. 6-6) and with paraffin (No. 6-8) operated quietly at first in contrast to their usual behavior but after a few hours the customary spalling and explosions were again evident.

A Globar heating element, coated with platinum (No. 6-2) operated with the cell voltage increasing rapidly after one hour of electrolysis and with a slight erosion of anode surface (see Table XXVIII).

Category No. 7 - Cast Silicon

A cast silicon metal rod (No. 7-1) polarized almost immediately. A rod of cast silicon metal that had been melted in a helium atmosphere (No. 7-2) behaved similarly, showing no erosion but polarizing rather rapidly (see Table XXIX).

Category No. 8 - Variations in Physical Dimensions

A sample of three thicknesses of Masonite, welded together by impregnation with silicon (No. 8-2) failed because the individual layers separated (see Table XXIX).

Category No. 9 - Coated Graphite or Carbon

Graphite rods coated with silicon carbide crystals (No. 9-1) eroded through the SiC coating, and then there was severe erosion of the graphite (see Table XXIX).

Category No. 10 - Miscellaneous

In this group, the carbonized Masonite (No. 10-2), the non-porous graphite heated in molten silicon (No. 10-4), and the R[illegible]x materials (No. 10-5 and 10-6) and the hot pressed beta silicon carbide (No. 10-9) eroded. The cold pressed silicon carbide recrystallized in helium (No. 10-3) and the Durhy No. 1 rods with no free carbon (No. 10-1) showed no appreciable erosion but operated at increasingly high cell voltage. The "dry shot" calcined extruded material gave erosion with final failure caused by an explosion breaking anode sample in half. (See Table XXX).

D. Tables

The following section contains Tables I through XXX, referred to in the preceding text.

TABLES

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TABLE I

LEAD DIOXIDE PLATING BATHS

Name: Acid Lead Nitrate

Code: LN-2

Lead Nitrate Concentration - 350 grams per liter; pH - 3.7

Preparation:

269 ml. of 69.9% nitric acid (266.5 g. HNO_3)
1000 ml. distilled water
472 g. lead oxide, PbO

Add the lead oxide slowly to the diluted nitric acid with stirring. Dilute to 2 liters, and head to 75°C. with stirring. Allow to cool and let stand for twelve hours. Filter through sintered glass.

Name: Alkaline Lead Tartrate

Code: 7M

Preparation:

100 g. potassium sodium tartrate, $KNaC_4H_4O_6 \cdot 4H_2O$
50 g. sodium hydroxide, NaOH
96 g. lead oxide, PbO

Dissolve in the order listed in distilled water to make 2 liters of solution. Heat to 60°C. to complete solution of lead oxide. Cool and let stand for 12 hours. Filter through sintered glass. Final pH is about 13.

Name: Lead Perchlorate

Code: LP-1

Preparation:

108 ml. of 60.3% perchloric acid (100 g. $HClO_4$)
167 ml. distilled water
111.0 g. lead oxide, PbO

First prepare 30% perchloric acid by diluting the 60% acid with the given volume of water. Then dissolve the lead oxide at room temperature. Add sufficient distilled water to make 2 liters. Heat to boiling for 2 to 3 minutes to dissolve white precipitate. Cool and use. Final pH is about 5.

(Continued)

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TABLE I (continued) (2)

Name: High Concentration Alkaline Lead Tartrate

Code: 7M (6X)

Preparation:

300 g. potassium sodium tartrate, $KNaC_4H_4O_6 \cdot 4H_2O$
150 g. sodium hydroxide, NaOH
288 g. lead oxide, PbO

Dissolve in the order listed in distilled water to make one liter of solution. Heat to 60°C. with stirring to complete solution of PbO. Cool and let stand for 12 hours. Filter through sintered glass. Final pH is about 13.

Name: High Concentration Lead Perchlorate

Code: LP-1 (4X)

Preparation:

216 ml. of 60.3% perchloric acid (200 g. $HClO_4$)
334 ml. distilled water
222 g. lead oxide, PbO

First prepare 30% perchloric acid by diluting the 60% acid with the given volume of water. Then dissolve the lead oxide at room temperature. Add sufficient distilled water to make one liter. Heat to boiling for about 3 minutes to dissolve any white precipitate formed. Cool and filter. Adjust pH to 2 with perchloric acid before use as lead dioxide plating bath.

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TABLE II

MASSIVE LEAD DIOXIDE ELECTRODES

Electrode No.	Plating Bath					Current Density Amps/Ft.²	Description of Base Material	Description of Plated Electrode	Plating Time		Physical Characteristics of Plated Electrodes			
	No.	$Cu(NO_3)_2 \cdot 3H_2O$ g/l	Gelatin g/l	Temp. °C.	Initial pH				Hours	Min.	Weight of Plate	Dimensions	Gms. PbO_2 Per Sq. Ft. of Surface	Lbs. PbO_2 Per Square Foot of Surface
191A	LN-2	--	--	69-73	Approx. 3.5	20	1/4"x6" copper foil (0.008" thick) cemented with DeKhotiosky cement to glass backing plate	Failed to obtain massive Plate as copper strip immersed in plating bath had almost completely eroded away.	19	75	--	--	--	--
191B	LN-2	Copper from previous erosion of copper strip present in bath	--	65-70	Less Than 1	20	1/4"x6" tantalum (0.012" thick) cemented with DeKhotiosky cement to glass backing plate	Hard, dense, smooth deposit extending over sides of glass plate. Large knobe formed at bottom, and side edges are thicker than main surface	165		Approx. 100 grams	3-1/2"High 3/4" wide-1/4" Ave. Thickness	--	--
191C	LN-2	5.6	--	60-70	Approx. 3.5	20	Platinum plated tantalum sheet with back and sides faced with plexiglass, 1" x4" of platinum plated tantalum immersed in plating bath.	Trees formed on plate which were removed daily from plate. Final plate had many nodules. This plate was not tested in cell as it cracked in half while machining.	142		332 grams Not incl. 247 gms. of trees which were removed.	--	--	--
191D	LN-2	Small amount introduced from copper cathode	--	58-63	Approx. 3.5	20	Monel sheet (0.05" thick) with back and sides faced with plexiglass, 5-3/4" x 1-1/16" of monel immersed in plating bath.	Monel sheet completely dissolved at surface level of plating bath. This plate was not tested in cell as it cracked in half when removed from Plexiglas jig.	89		204 grams	--	--	--
193	LN-2	--	--	72-76	Approx. 3.5	20	Tantalum rod 1/4" D. with 6-7/8" immersed in plating bath	Dark gray deposit with granular or crystalline surface very similar to the abrasive surface of #1 emery cloth.	42	13	120 grams	6-7/8"long 7/16" O.D.-3/32"thick	2325	5.13

(Continued)

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TABLE II, cont. (2)

Electrode No.	Plating Bath					Current Density Amps/Ft^2	Description of Base Material	Description of Plated Electrode	Plating Time		Physical Characteristics of Plated Electrode			
	No.	$Cu(NO_3)_2 \cdot 3H_2O$ g/l	Gelatin g/l	Temp. °C.	Initial pH				Hours	Min.	Weight of Plate	Dimensions	Gms. PbO_2 per Sq. Ft. of Surface	Lbs. PbO_2 Per Square Foot of Surface
194	LE-2	5.6	--	56-78	3.9	20	Monel screen with 5" x 3/4" area immersed in plating bath.	Heavy nodular growth along bottom and side edges. Deposit is hard. Monel screen partially dissolved at bath level.	73	30	278 grams	4-1/2" long-1-1/8" wide-3/16" thick	2760	6.04
195	LE-2	0.5		70-72	Approx. 3.5	20	Tantalum rod 1/4" D. x 7-1/8" long. #20 nickel wire coiled at top end before plating for electrical contact with electrodeposited PbO_2 in chlorate-perchlorate cell.	Similar in appearance to electrode No. 193; no lead plated on cathodes; copper plated on cathodes for 6-10 hours, then redissolves. Voltage drops as copper redissolves.	49	-	132 grams	7-3/8" long-7/16" O.D.-3/32" thick	2390	5.27
196	LE-2	Small amts. of nickel and copper from soln. of Monel sht. (Electrode No. 191D) and copper cathode.	--	60-70	4.6	20	50 mesh surgical tantalum gauze (0.003" wire) folded over to prevent sharp edges with 18 B&S nickel wire between folds as current lead. Nickel wire 1-1/2" below plating bath level. 1"x7" area of gauze in plating bath.	Heavy nodular growth as electrode No. 194 and granular surface as for #193.	117	45	788 grams	7-1/2" high-1-11/16" wide 1/4" thick	4490	9.90
197	LE-2	0.5	0.5	71-72	Approx. 3.5	20	Same as for Electrode #195	Gelatin has pronounced effect in reducing graininess of deposit, which however, is of much lower strength; cracked on normal handling.	45	15	161 grams	7-1/4" high-15/32" O.D.-7/64" thick	--	--
198	LE-2	0.5	0.5	70-75	3.7	60	Same as for electrode #195	Surface is dull with nodular growths on lower end. Deposit is stronger than #197. Intentionally broken for examination.	21	45	280 grams	7-1/4" high-7/16" O.D.-3/16" thick	--	--

(Continued)

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TABLE II, cont. (3)

Electrode No.	Plating Bath					Current Density Amps/ft^2	Description of Base Material	Description of Plated Electrode	Plating Time		Physical Characteristics of Plated Electrodes			
	No.	$Cu(NO_3)_2 \cdot 3H_2O$ g/l	Gelatin g/l	Temp. °C.	Initial pH				Hours	Min.	Weight of Plate	Dimensions	Gms. PbO_2 per Sq. Ft. of Surface	Lbs. PbO_2 Per Square Foot of Surface
199	LM-2	0.2	0.75	65-73	Approx. 3.5	30	1"x6"Tantalum sheet with #18 B&S nickel wire current leads threaded through holes in top portion of tantalum.	Plate blistered during early period of plating, finally plating over blisters. Intentionally broken for examination.	18		261 grams	--	--	--
200	LM-2	0.2	0.75	65-69	Approx. 1	20-25	Same as for electrode #199	No treeing. Edges only slightly larger than middle of plate. Knobs present at bottom corners and at nickel wire leads. Few cracks on edges at beginning of plating period where PbO_2 had pulled away from tantalum. Most of cracks covered over at end of plating period.	112	30	1400 grams	8-1/2"high 1-7/8"wide 5/8"thick	6690	14.7
201	LM-2	0.5	--	71-73	1.1	20	Same as for #195 except double nickel wire current lead.	Similar in appearance to #193; some copper plated on cathodes, but less than at initial pH of 3.5	51	30	236 grams	7-1/4"high 9/16"O.D. 5/32"thick	3685	8.13
202	LM-2	0.5	0.5	70-73	3.2	120	Same as for #195 & #201	Deposit had a dull sooty appearance. Heavy nodules on lower end and smaller nodules over entire surface which is very rough. Broken intentionally for examination.	5	55	142 grams	--	--	--
203	LM-2	0.5	--	70-72	0.6	30	Same as for #195 & #201	Similar in appearance to #195 No copper deposition on cathodes during PbO_2 plating.	28	30	133 grams	7-1/8"high 7/16"O.D. 3/32"thick	2490	5.62

(Continued)

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TABLE II, cont. (4)

Electrode No.	Plating Bath					Current Density Amps/ft²	Description of Base Material	Description of Plated Electrode	Plating Time		Physical Characteristics of Plated Electrodes			
	No.	$Cu(NO_3)_2 \cdot 3H_2O$ g/l	Gelatin g/l	Temp. °C.	Initial pH				Hours	Min.	Weight of Plate	Dimensions	Gms. PbO_2 per Sq. Ft. of Surface	Lbs. PbO_2 Per Square Foot of Surface
2044	LH-2	0.5	0.75	61-73	0.5	20	3" x 12" Tantalum screen (0.025" wire) with 1/4" nickel tubing and 18 B&S nickel wire current leads	Plating failed because 1/4" nickel tubing current leads eroded away. Lead dioxide plated well on nickel current leads but not on tantalum in area between nickel tubing current leads. Intentionally broken.	49	30	950 grams	--	--	--
2061	LH-2	0.5	0.75	68-69	Less than 0.5	20	3" x 12" Tantalum screen (0.025" wire) with 20 B&S nickel wire current leads	Poor plate on tantalum around nickel wire current leads. Heavier plate on bottom portion. Some knobs present on bottom and sides.	119	18	2927 grams	8" long 4-1/2" wide		
295	LH-2	0.5	--	68-72	0.6	30	Tantalum U-tube, 9/32" O.D. 7/8" R. U-bend, 20 B&S nickel wire coiled around top ends of both arms.	Similar in appearance to #193	30	30	336 grams	5-3/4" long 9/16" O.D. 7/64" thick	3505	7.72
2063	LH-2	0.5	0.75	70	4.8	20	As for #2063, except 22 of #16 B&S nickel wires sandwiched between folded tantalum screen for 2" at top for current leads.	Good PbO_2 deposit on nickel, but treeing and incomplete coverage on tantalum.	23	0	--	--	--	--
2068	LH-2	0.5	0.75	67-72	4.7	25	As for #2064.	Treeing and incomplete coverage of anode. Cathodes covered with insulating glaze of lower lead oxides.	24	0	--	--	--	--
2065	LH-2	1.5	0.75	67-71	3.2	25	As for #2064, except only tantalum immersed in plating bath.	Treeing at lower edge of anode. PbO_2 deposit otherwise of good quality.	24	0	--	--	--	--
297	[illegible](2)	3.8 of copper carbonate	--	73-76	13	10	Tantalum rod, 1/4" D. x 7" immersed in bath.	Heavy white ppt. formed in plating bath; PbO_2 has some nodules.	60	-	--	--	--	--

(Continued)

TABLE II, cont. (5)

Electrode No.	Plating Bath					Current Density Amps/ft²	Description of Base Material	Description of Plated Electrode	Plating Time		Physical Characteristics of Plated Electrodes			
	No.	$Cu(NO_3)_2 \cdot 3H_2O$ g/l	Gelatin g/l	Temp. °C.	Initial pH				Hours	Min.	Weight of Plate	Dimensions	Gms. PbO_2 Per Sq. In. of Surface	Lbs. PbO_2 Per Square Foot of Surface
208	LR-2	15	0.75	69-72	1.8	20	As for #204, except #16 B&S nickel twisted into top 3" of tantalum screen. Current contact made to tantalum only, not nickel.	Uniform, complete coverage, except for nodules along edges	97	45	- -	10-1/2"long 3-1/8"wide 3/8" thick	- -	- -
209	LR-1 (4X)	-	- -	69-73	2	20	As for #195, except use #16 B&S nickel wire.	Smooth, satiny deposit.	49	-	185 g.	5" long 0.D. 3/4" thick	3588	7.89
210	LR-2	(A) 2-5	1.25	69-72	1.5	20	3" x 18" tantalum screen, 14 mesh, 0.025" wire with two 6" woven with #16 B&S nickel wire current leads	Top portion of screen with nickel wires plated as (A). Other end then plated as (B) with 4" overlap on 1st PbO_2 deposit. Nickel wires eroded.	(A)73	-	- -	18" long 3-1/2" wide 1/2" thick	- -	- -
		(B) 2-5	1.40	67-73	1.5	20			(B)120	-	- -		- -	- -
211	LR-1 (4X)	-	- -	69-73	2	20	As for #209, tantalum rod.	Smooth, satiny deposit.	48	-	104 g.	5" long 0.D. 3/4" thick	2980	5.71
212	LR-2	1.0	0.75	70-73	1.1	20	As for #209, tantalum rod.	Smooth, adherent deposit, but with many deep gas holes in surface.	4	-	- -	- -	- -	- -
213A	LR-2	-	0.75	68-70	1.1	20	As for #209, tantalum rod.	Anode grazing in bath; PbO_2 deposit peels.	1	-	- -	7-1/8" long	- -	- -
213B	LR-2	-	0.75	68-70	1.05	20	As for #209, tantalum rod.	As for #213A	2	-	- -	7-1/8" long	- -	- -
213C	LR-2	-	0.75	73-75	1.2	10	As for #209, tantalum rod.	As for #213A. Nickel wire also eroded.	16	-	- -	7-1/8" long	- -	- -
213D	LR-2	-	0.75	69-72	2.3	10	As for #209, tantalum rod.	As for #213A.	2		- -	7-1/8" long	- -	- -
214	LR-2	-	- -	70-72	3.8	20	As for #209, tantalum rod.	No grazing during plating. PbO_2 deposit same as for #193	37	15	143 g.	7-1/8" long 15/32" O.D. 7/64" thick	3510	5.53
215	LR-2	-	- -	68-71	3.1	20	As for #209, tantalum rod.	As for #214.	44	48	189 g.	7-1/8" long 15/32" O.D. 7/64" thick	2610	5.75
216	LR-2	-	- -	68-71	3.5	20	As for #209, tantalum rod.	As for #214.	29	-	123 g.	7-1/8" long 7/16" O.D. 3/32" thick	2260	5.98

(Continued)

TABLE II. cont. (6)

Electrode No.	Plating Bath					Current Density Amp/ Ft²	Description of Base Material	Description of Plated Electrode	Plating Time		Physical Characteristics of Plated Electrodes			
	No.	$Cu(NO_3)_2 \cdot 3H_2O$ g/l	Igepal CO-880 g/l	Temp. °C.	Initial pH				Hours	Min.	Weight of Plate	Dimensions	Gms. PbO_2 Per Sq. Ft. of Surface	Lbs. PbO_2 Per Square Foot of Surface
217	LE-2	-	0.75	68-69	3.5	20	As for #209, tantalum rod	PbO_2 Surface smoother than with no surface active agent. PbO_2 much stronger than when gelatin used, and somewhat stronger than when no surface active agent used.	26	-	91 g.	7-1/4" long 13/32" O.D 5/64" thick	2120	4.67
218	LE-2	0.25	0.75	68-72	2.8	15	Tantalum screen, 3" x 18". As for #210. Current contact to tantalum only.	PbO_2 very hard. Some nickel wires eroded. Treeing at edges eliminated by use of shields.	116	-	3635 g.	14" long 3-1/2" wide 1/2" thick	5350	11.77
219	LE-2	0.25	0.75	70-73	2.2	15	Tantalum screen alone (no nickel wires attached) 3" x 18", 14 mesh screen with 0.025" wire.	PbO_2 very hard. Plexiglas shields used to eliminate treeing at side and bottom edges.	142	30	4500 g.	14-1/2" long 3-1/2" wide 5/8" thick	6990	14.1
220	LE-2	0.25	0.75	70-76	2.9	15	Spectrographic grade graphite rod, 1/4" diam.	PbO_2 deposit is similar to that on tantalum rod.	45	25	140 g.	7-1/4" long 7/16" diam.	2660	5.86
221	LE-2	0.25	0.75	70-76	2.9	15	As for #220, graphite rod.	As for #220, except for several shallow grooves near bottom due to anodic erosion.	41	25	116 g.	7-1/4" long 7/16" diam.	2210	4.87
222	LE-2	0.25	0.75	70-73	2.6	15	Durhy #2 rod, 7/16" diam. x 9-1/2" long.	PbO_2 surface is very uneven due to surface grooves in Durhy starting rod.	47	20	354 g.	6-7/8" long 3/4" diam.	3220	7.09
223	LE-2	0.25	0.75	70-72	2.2	15	Tantalum rod, 1/4" diam. x 9" long.	PbO_2 deposit is hard and smooth.	50	-	155.8 g.	7-1/4" long 15/32" diam.	2700	5.95
224	LE-2	0.25	0.75	70-72	2.1	15	As for #223, tantalum rod.	About same as #223.	50	-	154 g.	7-1/4" long 15/32" diam.	2700	5.95
225	LE-2	0.75	0.75	69-71	2.2	15	As for #222, Durhy #2 rod.	About same as #222.	48	50	317.1 g.	8-1/2" long 3/4" diam.	2880	6.35
226	LE-2	0.25	0.75	70	2.2	15	As for #223, tantalum rod.	About same as #223.	51	50	251.8 g.	7-1/4" long 9/16" diam.	3590	7.91
227	LE-2	0.25	0.75	70	2.2	15	As for #223, tantalum rod.	About same as #223.	51	50	221.2 g.	7-1/4" long 9/16" diam.	3430	7.55
228	LE-2	0.75	0.75	70-74	2.0	15	As for #223, tantalum rod.	About same as #223.	51	40	129.9 g.	6" long 1/2" diam.	2640	5.82
229	LE-2	0.75	0.75	70-73	2.0	15	As for #223, tantalum rod.	About same as #223.	51	40	126.9 g.	6" long 1/2" diam.	2580	5.68

(Continued)

TABLE II cont. (7)

Electrode No.	Plating Bath No.	$Cu(NO_3)_2 \cdot 3H_2O$ g/l	Igepal CO-880 g/l	Temp. °C.	Initial pH	Current Density Amps/Ft^2	Description of Base Material	Description of Plated Electrode	Plating Time Hours	Plating Time Min.	Physical Characteristics of Plated Electrodes: Weight of Plate	Dimensions	Gms. PbO_2 Per Sq. Ft. of Surface	Lbs. PbO_2 Per Sq. Ft. of Surface
230	LM-2	0.75	0.75	68-73	2.3	15	As for #222, Durby #2 red.	About same as #222.	44	55	277.6 g.	8-1/2" long 11/16" diam	5310	7.30
231	LM-2	0.75	0.75	71-77	2.7	20	Tantalum screen, 2" x 12", 14 mesh screen with .025" wire.	PbO_2 very hard. Plexiglas shields used to eliminate treeing at side and bottom edges.	91	50	1859 g.	9-1/2" long 2-3/8" wide 3/8" thick	5910	13.0
232	LM-2	0.75	0.75	72-77	2.5	15	Tantalum sheet, .003" thick.	Tantalum polarized in 5 min. Cleaning with 50% HF only temporarily corrected this polarizing. PbO_2 formed unevenly due to slow polarization.	70	-	-	14-1/2" long 3" wide 1/4" thick	-	-
233	LM-2	0.75	0.75	70-72	2.9	15	As for #232, but tantalum first grit blasted to remove oxide to give a brittle, dull sheet roughened with many craters.	PbO_2 was deposited at a low steady voltage to a 1/2" dia. thickness without polarization. Roughness of base repeated by PbO_2. Plexiglas shields used.	91	25	3378 g.	14-1/2" long 3" wide 1/2" thick	-	-
234	LM-2	0.75	0.75	71-74	2.9	15	As for #232, but plating attempted on only one side by cementing tantalum to sheet of Plexiglas.	Tantalum buckled into cosine shape along vertical axis. Tantalum polarized in 22 hrs. since oxide film was not first removed.	22	-	-	14-1/2" long 3" wide	-	-
235	LM-2	0.75	0.75	70-74	2.8	20	Nickel screen, 3" x 18", 8 mesh with .028" wire.	PbO_2 plated on one side by backing screen with Plexiglas. Nickel screen along top edge eroded away as PbO_2 thickness reached 1/8".	95	-	-	16" long 3-3/8" wide	-	-
236	LM-2	0.75	0.75	70-75	2.8	15	As for #232, but tantalum oxide first removed by rubbing with 3/ emery and crocus cloths.	PbO_2 deposited without polarization. Plexiglas shields used.	117	30	5367 g.	15-5/8" long 4-1/2" wide 9/16" thick	7150	15.8

(Continued)

TABLE II. cont. (B)

Electrode No.	Plating Bath					Current Density Amps/ Ft^2	Description of Base Material	Description of Plated Electrode	Plating Time		Physical Characteristics of Plated Electrodes			
	No.	$Cu(NO_3)_2 \cdot 3H_2O$ g/l	Igepal CO-880* g/l	Temp. °C.	Initial pH				Hours	Min.	Weight of Plate	Dimensions	Lbs. PbO_2 Per Sq. Ft. of Surface	Lbs. PbO_2 Per Sq. Ft. of Surface
237	LK-2	0.75	0.75	70-78	2.7	20	Nickel screen, 3" x 16", 16 mesh with .012" wire.	PbO_2 plated on only one side as was done for #235; also PbO_2 did not grow symmetrically, but was much heavier along edges.	75	30	-	16" long 7" wide 3/16" thick	-	-
238	LK-2	[illegible]	[illegible]	72-82	2.7	20	As for #237.	PbO_2 plated on both sides, and Plexiglas baffles used. Nickel protected at solution level by coating of stop-off lacquer.	137	45	6825 g.	15-3/4" long 3-1/2" wide 7/8" thick	9058	19.9

* Igepal CO-880 (Alkyl phenoxy polyoxyethylene ethanol)
Antara Products Division of General Dyestuff Corporation, New York, N.Y.

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TABLE LII

SURFACE-ACTIVE AGENT SCREENING TESTS
Plating Bath - LN-2 (Lead Nitrate)
Surface Active Agent Concentration-0.75 g/l., except when otherwise noted
Anode Current Density - 20 Amp/Ft.^{2}
Anode - Tantalum Rod, 1/4" D.

AGENT	TYPE	CLOUD POINT IN LN-2, °C.	QUALITY OF PbO_2 DEPOSITED
Triton X-100	Non-ionic	77	Triton X-100 separates as an oil after 10-20 hours plating. PbO_2 smoother than with no agent, and stronger than when gelatin used.
Ethomeen C/15	Cationic	Clear to 92	Poor, non-homogeneous PbO_2 deposit.
Nacconol NRSF	Anionic	<0.3 g/l soluble even at 90°C.	- - - -
Igepal CO-430	Non-ionic	40	- - - -
Igepal CO-630	Non-ionic	70	- - - -
Igepal CA-710	Non-ionic	77	- - - -
Igepal CO-850	Non-ionic	Clear to 95	PbO_2 had larger grained crystalline surface than from bath with Triton X-100, but stronger in resisting fracture.
Igepal CO-880	Non-ionic	Clear to 95	PbO_2 had about same size grained crystalline surface as from bath with Triton X-100. Deposit is dense, free of internal cracks, and very strong
Santomerse #1 (40% active)	Anionic	Heavy $PbSO_4$ ppt. from Na_2SO_4 content	Ppt filtered off before plating. PbO_2 smoother than from bath with Triton X-100, but not as strong.
Santomerse #3 (100% active)	Anionic	<0.3 g/l soluble even at 90°C.	- - - -

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TABLE IV

X-RAY DIFFRACTION AND SPECTROGRAPHIC ANALYSES OF MASSIVE LEAD DIOXIDE DEPOSITS

Plate No.	L.N.B. Reference	XRD Analysis	Spectrographic Analysis	
			Major	Minor
191C	1365:94-97	PbO_2	Pb	Al, Mg, Cu, Fe
193	1367:102	PbO_2	Pb	Mn, Ca, Mg
194	1367:111,2	PbO_2	Pb	Ni, Cu, Mg, Ca
197	1367:139-41	PbO_2	Pb	Ca, Cu, Ni, Al, Mg
198	1365:175	PbO_2	Pb	Ni
199	1365:175	PbO_2	Pb	Al, Ag, Fe, Bi, Te

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TABLE V

CURRENT EFFICIENCIES IN CHLORATE-PERCHLORATE CELL WITH MASSIVE LEAD DIOXIDE ANODES

(See Table II for Description of Electrodes)

ELECTRODE NO.	TEST NO.	ANODE CURRENT DENSITY A./cm.^{2}	$NaClO_3$ CONC. RANGE OVER WHICH CURRENT EFFICIENCY WAS CALCULATED		CURRENT EFFICIENCY OVERALL %	CURRENT EFFICIENCY DOWN TO 100 g./l. $NaClO_3$, %	CELL TEMP. °C.	CELL pH	Ml 0.5 N $HClO_4$ ADDED TO MAINTAIN pH
			INITIAL g./l.	FINAL g./l.					
191	1	0.1	596	429	49.9		2	5	5.7
	2	0.1	632	Not Analyzed				9	
193	1	0.1	632	505	45.2		3.5	6	10.5
	2	0.1	616	427.5	44.1		3	6	11.5
	3	0.1	616	43.8	52.8	57.4	2.5	3	18.0
194	1	0.1	632	109	48.9	48.9	5	3.5	2.7
	2	0.1	616	124	37.8	37.8	5	3	5.0
195	1	0.1	616	336	51.7		2.5	4	15.5
	2	0.1	616	83.3	49.1	49	2	3	19.5
	3	0.1	616	168.6	52.5		1.5	3	13.0
	4	0.2	605	59.6	64.9	66.4	6.5	1.6	0
	5	0.2	605	63.8	71.0	73.3	7	1.7	0
	6	0.2	605	32.3	69.4	84.6	8	5	0
	7	0.2	605	77.4	84.0	87.2	6	1.0	0
	8	0.3	662	Not Analyzed					
	9	0.3	603	96.8	81.2	81.2	4	7	0
196	1	0.1	616	28	38.6	38.8	10	4	18.0
	2	0.1	616	20.7	48.1	53.0	10	3.5	20.0
	3	0.1	616	69	46.0	48.3	9.5	3.5	28.0
	4	0.1	605	24.8	50.3	59.5	11	0.9	5.0
	5	0.1	605	59.1	63.2	64.4	10	1.8	0
	6	0.1	605	4.4	50.9	71.8	10	1.0	0
	7	0.1	605	263	86.1		10	3	0
	*8	0.1	605	3.5	74.5	81.2	12	4.3	0
	*9	0.1	603	23.6	70.1	76.7	16	9.5	0
	*10	0.1	603	76.8	65.1	66.0	21	10	0
	*11	0.1	603	116.5	55.0	55.0	9	10	0

* - Cell electrolyte contained 2.5 g. sodium fluoride per liter.

Continued

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TABLE V, cont. (2)

ELECTRODE NO.	TEST NO.	ANODE CURRENT DENSITY A./cm.^{2}	$NaClO_3$ CONC. RANGE OVER WHICH CURRENT EFFICIENCY WAS CALCULATED		CURRENT EFFICIENCY OVERALL %	CURRENT EFFICIENCY DOWN TO 100 g./l. $NaClO_3$, %	CELL TEMP. °C.	CELL pH	Ml. 0.5 N $HClO_4$ ADDED TO MAINTAIN pH
			INITIAL g./l.	FINAL g./l.					
200	1	0.2	550	319	83.2		6	10.2	0
	2	0.2	606.5	49	75.8	78.4	10	10.5	0
201	1	0.2	605	96.2	61.7	61.7	7.5	1.4	0
	2	0.2	605	72.7	65.0	68.8	7.5	0.9	0
	3	0.2	662	Not Analyzed					
	4	0.2	603	103	80.3	80.3	3	6.5	0
	5	0.2	603	111	77.7	77.7	5	9	0
	6	0.3	608	180.5	71.3		3	10	0
	7	0.3	608	83.9	64.2	65.1	9	9.5	0
	8	0.3	608	162	81.6		6	8.5	0
	9	0.45	602	129	43.6	43.6(-)	16	10	0
	10	0.45	602	77.4	60.6	60.6	15	9	0
	11	0.45	602	109.6	56.8	56.8	12	9	0
	12	0.45	602	43.2	72.1	78.3	48	10	0
	13	0.45	601	32.3	73.2	81.7	46	9.5	0
	14	0.45	601	59.7	70.1	75.1	46	9.7	0
	15	0.3	601	51.6	67.9	70.8	52	9.2	0
	16	0.3	601	77.5	66.7	68.4	48	9.2	0
	17	0.3	601	65.9	67.0	70.2	49	9.3	0
	18	0.2	582	53.3	66.2	72.2	49	8.5	0
	19	0.2	582	70.6	73.6	76.3	48	9.5	0
	20	0.2	582	68.3	63.3	69.0	48	8.8	0
	21	0.23	679	133.5	58.3	58.3	48	9.5	0
	22	0.3	755	103.3	70.8	70.8	53	9.0	0
	23	0.3	582	109.7	74.2	74.2	49	3.	9

(Continued)

TABLE I. cont. (3)

ELECTRODE NO.	TEST NO.	ANODE CURRENT DENSITY A/cm.^{2}	$NaClO_3$ CONC. RANGE OVER WHICH CURRENT EFFICIENCY WAS CALCULATED		CURRENT EFFICIENCY OVERALL %	CURRENT EFFICIENCY DOWN TO 100 g./l. $NaClO_3$, %	CELL TEMP. °C.	CELL pH	Ml. 0.5 N $HClO_4$ ADDED TO MAINTAIN pH
			INITIAL g./l.	FINAL g./l.					
203	1	0.2	608	121.3	63.8	63.8	7	5	55
	2	0.2	608	64.5	61.7	62.7	6	4	24
	3	0.2	602	87	59.3	59.8	10	4.5	30
	4	0.3	602	100.5	58.0	58.0	11	3	17
	5	0.3	602	64.6	61.9	64.1	9	4	15
	6	0.3	602	121	58.6	58.6(-)	16	6	27
205	1	0.2	603	87.5	62.3	63.9	13	8.5	0
	2	0.2	603	168.5	53.8		17	4.5	0
	3	0.3	603	65	59.3	61.3	15	9.5	0
	4	0.2	608	93.2	60.0	60.0	10	10	0
	5	0.2	608	28.1	49.6	55.1	16	10	0
	6	0.2	608	98.2	65.1	65.1	12.5	4	56
209	1	0.2	602	64.5	47.5	48.4	8	9	0
	2	0.2	602	90.5	61.0	61.9	7	4	37
	3	0.2	602	47.2	71.4	77.7	45	10	0
	4	0.2	601	67.8	68.7	70.9	46	9.6	0
	5	0.2	601	75.8	68.1	69.6	48	9.5	0
215	1	0.15	601	132	46.9		9.5	5	31
	2	0.2	601	93.5	62.1	62.5	9	4	23
	3	0.2	601	69	64.0	66.6	8	4.5	16
	4	0.3	582	50.2	62.5	66.5	9	5.7	21
	5	0.3	582	79.6	71.7	73.7	9	4	19
	6	0.3	582	38.9	67.0	74.0	8.7	3.6	9
	7	0.45	582	59	65.4	68.8	10	4.5	18
	8	0.45	582	53.3	67.8	72.4	10	2.5	4
	9	0.30	582	83.2	78.2	79.6	49	7	32
	10	0.30	597	55.2	69.2	74.3	46	3	11

(Continued)

TABLE V. cont. (4)

ELECTRODE NO.	TEST NO.	ANODE CURRENT DENSITY A./cm.^{2}	$NaClO_3$ CONC. RANGE OVER WHICH CURRENT EFFICIENCY WAS CALCULATED		CURRENT EFFICIENCY OVERALL %	CURRENT EFFICIENCY DOWN TO 100 g./l. $NaClO_3$, %	CELL TEMP. °C.	CELL pH	Ml. 0.5 N $HClO_4$ ADDED TO MAINTAIN pH
			INITIAL g./l.	FINAL g./l.					
216	1	0.2	601	93.6	62.6	63.0	51	9.2	0
	2	0.2	601	90.4	65.0	66.2	47	9.3	0
	3	0.2	601	84.8	64.8	67.1	48	9.2	0
	4	0.3	582	135	56.0		50	9.1	0
	5	0.3	582	87.1	71.2	72.0	49	9.4	0
	6	0.3	582	91.3	60.6	61.3	49	8.9	0
221	1	0.3	602	261	46.6		49	9.7	0
	2	0.3	602	88.4	60.8	62.2	45	9.6	0
	3	0.3	602	38.9	76.7	84.2	44	9.5	0
	4	0.3	602	32.4	65.0	76.5	45	9.5	0
222	1	0.3	602	98.7	69.3	69.3	28	9	0
223	1	0.3	602	97.7	57.5	57.5	45	9	0
	2	0.3	602	56.0	64.3	73.5	35	9	0
	3	0.3	602	56.3	61.5	66.7	26	9	0
	4*	0.3	607	155	16.6	-	25	3	0
226	1	0.3	602	58.9	51.1	55.1	35	9	0
	2	0.3	602	42.1	63.2	72.5	25	9	0
	3**	0.3	607	43.8	58.4	69.0	26	1.3	0
	4**	0.3	607	26.5	52.1	62.5	26	-	0
227	1	0.3	602	87.5	48.6	49.0	35	9	0
	2	0.3	602	79.5	58.9	63.0	25	9	0
	3***	0.3	607	16.4	61.2	78.0	26	8.9	0
	4***	0.3	607	24.7	52.3	66.7	26	9	0
230	1	0.3	602	129	65.1	-	27	9	0

NOTES: 1 - Current efficiencies to 100 g. $NaClO_3$ per liter were interpolated from data, assuming linear variation over a short range.

2 - Electrode 205 was cooled by flowing 10°C. water through the tantalum U-tube core for the first two runs.

3 - Grams $HClO_4$ (100%) = Ml. 0.5 N $HClO_4$ x .0502.

* - Cell electrolyte contained 5.0 g. sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$, per liter.

** - Cell electrolyte contained 1.0 g. sodium thiocyanate, NaSCN, per liter.

*** - Cell electrolyte contained 2.5 g. sodium fluoride, NaF, per liter.

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TABLE VI

SUMMARY OF LEAD DIOXIDE ANODE CURRENT EFFICIENCIES IN CHLORATE-PERCHLORATE CELL

ANODE CURRENT DENSITY A./cm.^{2}	CELL TEMP. °C.	CELL pH	AVERAGE CURRENT EFFICIENCY IN $NaClO_3$ CONC. RANGE OF 600-100 g/l-%	ELECTRODE NUMBERS INCLUDED (SEE TABLE V)
0.1	2-11	0.9-4	52.9	193, 194, 195, 196 (10 tests)
0.2	3-16	0.9-6.5	68.9	195, 201, 203, 205, 209, 215 (14 tests)
		8.5-10.5	66.1	200, 201, 205 (6 tests)
	45-51	8.5-10	67.6	201, 209, 216 (10 tests)
0.3	4-28	3-6	65.8	203, 215 (6 tests)
		7-9.5	66.7	195, 201, 222, 223, 226, 227 (7 tests)
	44-53	3-7	76.0	201, 215 (3 tests)
		8.9-9.4	68.2	201, 216, 221, 223, 226 (12 tests)
0.45	10-16	2.5-4.5	70.6	215 (2 tests)
		9-10	53.7	201 (3 tests)
	48	9.5-10	78.4	201 (3 tests)

NOTE: These results are a summary of data of Table V.

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TABLE VII

CURRENT EFFICIENCIES IN 100 AMPERE CELL WITH MASSIVE LEAD DIOXIDE ANODE #219

TEST NO.	CURRENT AMP.	ANODE CURRENT DENSITY AMP./CM.^{2}	NaCl CONC. RANGE OVER WHICH CURRENT EFFICIENCY WAS CALCULATED		CURRENT EFFICIENCY OVER-ALL - %	CURRENT EFFICIENCY DOWN TO 100 g/l $NaClO_3$ %	CELL TEMP. °C.	CELL pH	NOTES
			INITIAL g/l	FINAL g/l					
219-1	80	0.24	610	75.8	35.0	37.4	52	9.8	Cell cooling by refrigerating bath water surrounding cell.
219-2	80	0.24	610	20.7	43.3	48.8	50	9.2	Cell cooling by refrigerating bath water surrounding cell.
219-3	100	0.28	610	60.3	43.2	45.7	45	9.5	Cell cooling by refrigerating bath water surrounding cell.
219-4	100	0.28	597	25.8	42.3	52.1	32	10.0	Tap water through glass cooling coils immersed in cell, from 219-4 on.
219-5	100	0.29	597	70.6	52.5	-	32	9.4	Water to adjust electrolyte level added only at end of run.
219-6	100	0.29	609	158.2	48.4	-	30	9.2	Ditto; electrolyte agitated with power stirrer.
219-7	100	0.28	609	92	45.4	45.7	30	9.5	Electrolyte stirred; water added at frequent intervals in this and following runs.
219-8	100	0.28	609	104.8	51.5	51.5	30	9.7	No stirring of electrolyte in this and following runs.
219-9	100	0.28	609	106	50.8	50.8	32	9.5	
219-10	75	0.21	609	29.8	43.3	51.5	38	9.6	Plexiglas baffles placed between anode and cathodes.
219-11	75	0.21	609	73.3	39.1	41.6	31	10.0	Check run at same anode current density without baffles.
219-12	100	0.28	609	89.6	44.9	45.4	31	9.9	
219-13	100	0.29	609	133.6	54.1	51	32	9.9	Water added only at end of run.
219-14	100	0.29	609	92.2	44.3	44.5	31	9.8	Water added only at end of run.
219-15	100	0.29	606	74	46.1	48.4	29	9.9	Water added only at end of run.
219-16	100	0.28	602	30.6	34.6	44.7	27	9.2	
219-17	100	0.28	Incomplete run of 2.7 hours				22 to 64	9.7	

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(Continued)

TABLE VII. cont.

TEST NO.	CURRENT AMP.	ANODE CURRENT DENSITY AMP./CM.^{2}	NaCl CONC. RANGE OVER WHICH CURRENT EFFICIENCY WAS CALCULATED		CURRENT EFFICIENCY OVERALL - %	CURRENT EFFICIENCY DOWN TO 100g/l $NaClO_3$ %	CELL TEMP. °C.	CELL pH	NOTES
			INITIAL g/l	FINAL g/l					
219-18	100	0.28	602	130.6	40.1	-	46	9.8	
219-T19	100	0.28	580	103.4	27.4	27.4	43	9.3	Electrolyte made with Pennsalt technical grade $NaClO_3$ containing 0.08% $Na_2Cr_2O_7 \cdot 2H_2O$
219-20	100	0.28	602	55.6	52.6	60.4	33	-	
219-T21	100	0.28	579	82.2	25.1	26.7	35	-	As for 219-T19.
219-22	100	0.28	607	102	24.8	24.8	35	5.1	1.2 g/l $Na_2Cr_2O_7 \cdot 2H_2O$ added to electrolyte; this is equivalent to 0.2% on dry $NaClO_3$ basis.
219-23	100	0.28	607	15.7	39.2	59.0	31	8.8	
219-24	100	0.28	612	1.2	28.8	64.3	33	-	

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TABLE VIII

WEIGHT LOSSES OF LEAD DIOXIDE ANODES IN CHLORATE-PERCHLORATE CELL

ELECTRODE NUMBER	TEST NUMBER	CELL OPERATION-HOURS	CELL CURRENT AMP.	CURRENT DENSITY A./cm^2	WEIGHT CHANGE g.	GRAMS WT. LOSS PER 10,000 AMP.-HRS. PRODUCTION OF 25.2 LBS. $NaClO_4$ AT 50% CURRENT EFFICIENCY	GRAMS WT. LOSS PER TON $NaClO_4$ FORMED AT 50% CURRENT EFFICIENCY
193	1,2,3	311	3.2	0.1	+0.02	None	None
195	1,2,3	430	3.2	0.1	-0.06	0.[illegible]	34.6
	4	72.8	6.4	0.2	-0.03	0.64	51.0
	5,6,7	191.7	6.4	0.2	-0.05	0.41	32.4
	1 to 7	694.5			-0.14	0.46	36.2
196	1,2,3	238.8	10	0.1	+0.58	None	None
	4,5,6,7	214.3	10	0.1	+0.24	None	None
	8,9,10,11	201.0	10	0.1	-0.57	2.83	225*
	1 to 11	654.1	10	0.1	+0.25	None	None
201	1,2	142.6	6.4	0.2	+0.015	None	None
	3	21.4	6.4	0.2	-0.25	18.2	1440**
	4,5	108.9	6.4	0.2	-0.024	0.34	27.3
	6,7,8	169.9	6.4	0.3	+0.012	None	None
	9,10,11	244.0	6.4	0.45	-0.105	0.67	53.3
	12,13,14	201	6.4	0.45	+0.019	None	None
	15,16,17	207	6.4	0.30	-0.056	0.42	33.5
	18,19,20	200	6.4	0.20	+0.056	None	None
	21,22	153	6.4	0.30	+0.060	None	None
	1 to 22	1447.8	6.4		-0.273	0.30	23.8
203	1,2,3	223.8	6.4	0.2	+0.017	None	None
	4,5,6	221	6.4	0.3	-0.001	0.007	0.56
	1 to 6	444.8	6.4		+0.016	None	None
205	3,4,5,6	224.8	10	0.2	+0.491	None	None
209	1,2	170.7	6.4	0.2	+0.139	None	None
	3,4,5	201	6.4	0.2	-0.289	2.24	178**
	1 to 5	381.7	6.4		-0.150	0.61	48.2
215	1,2,3	229	6.4	0.2	+0.055	None	None
	4.5.6	204	6.4	0.3	+0.012	None	None
	7,8	137	6.4	0.45	-0.022	0.25	19.9
	1 to 8	570	6.4		+0.045	None	None

(Continued)

TABLE VIII, cont. (2)

ELECTRODE NUMBER	TEST NUMBER	CELL OPERATION - HOURS	CELL CURRENT AMP.	CURRENT DENSITY A/cm^2	WEIGHT CHANGE g.	GRAMS WT. LOSS PER 10,000 AMP.-HRS. → PRODUCTION OF 25.2 LBS. $NaClO_4$ at 50% CURRENT EFFICIENCY	GRAMS WT. LOSS PER TON $NaClO_4$ FORMED AT 50% CURRENT EFFICIENCY
216	1,2,3	207	6.4	0.2	-0.020	0.15	12.0
	4,5,6	200	6.4	0.3	-0.031	0.24	19.2
	1 to 6	407	6.4		-0.051	0.20	15.5
226	3,4	125.7	10	0.3	-0.019	0.15	12.0
227	3,4	125.7	10	0.3	-0.036	0.29	22.7

FOOTNOTES:

* Weight loss due largely to mist corrosion of Wood's metal casting around current contact area. Electrolyte contained 2.5 g./l. of sodium fluoride.

** Chips of PbO_2 broken loose from top of anode.

TABLE IX

TESTING OF CURRENT LEADS TO MASSIVE LEAD DIOXIDE ANODES IN CHLORATE-PERCHLORATE CELL

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Plate No.	Test No.	Description of Current Lead	Observations
191B	1	Universal clip (Mueller Electric Co.) direct to lead dioxide-wrapped with No. 33 electrical tape to protect clip from cell spray.	Anode ran warm-clip corroded by electrolyte spray and seepage.
191B	2	Brass plates to lead sheet to lead dioxide, screw to tighten assembly. Assembly covered with wax.	Current lead operated warm. Finally lead dioxide cracked under the brass plate pressure. Evidence of reaction between lead sheet and brass plates and between lead sheet and lead dioxide.
193	1	Sheet copper wrapped around lead dioxide plated on tantalum rod. Sheet copper tightened against lead dioxide with hose clamp. Current lead soldered to sheet copper. Assembly covered with No. 33 electrical tape.	Current lead ran warm. No attack or corrosion.
193	2&3	18 B&S copper wire tightly wound around lead dioxide on tantalum rod. Wood's metal cast around copper wire with ends of copper wire through Wood's metal as external lead.	Operated satisfactorily but there was slight corrosion of Wood's metal by electrolyte spray.
194	1&2	18 B&S nickel wire tightly wound around lead dioxide plated on Monel screen. Wood's metal cast around nickel wire with ends of nickel wire through Wood's metal as external lead.	Operated satisfactorily but there was slight corrosion of Wood's metal by electrolyte spray. Portion of Monel screen below electrolyte level and within lead dioxide was completely eroded away.
195	1 thru 9	20 B&S nickel wire tightly wound around tantalum rod with one end of nickel wire as external current lead. Lead dioxide plate over tantalum and nickel wire.	Operated satisfactorily at slightly lower cell voltage (0.2 to 0.3 volts) than Plate No. 193, Tests 2 and 3.
196	1 thru 11	18 B&S nickel wire between folds of tantalum gauze with four nickel wire external leads-Lead dioxide plated over tantalum and nickel wire. Wood's metal cast at top of plate to hold nickel wire external leads rigid.	Operated satisfactorily; some corrosion of Wood's metal.

(Continued)

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TABLE IX.(Cont.) (2)

Plate No.	Test No.	Description of Current Lead	Observations
200	1A2	18 B&S nickel wires threaded through holes in top portion of 1" x 8" tantalum sheet. PbO_2 plated over this assembly to 5/8" total thickness. Zinc metal spray coated over top 2 inches then a block of Wood's metal 1" x 2-1/2" x 2" cast over this area. Free ends of nickel wire looped over and embedded in Wood's metal.	Operated smoothly at 25 amperes; some corrosion of Wood's metal.
201, 202, 203, 205, 209, 215, 216	All	20 B&S nickel wire tightly wound around tantalum rod with two ends of nickel wire as external current leads. Lead dioxide plate over tantalum and nickel wire.	Operated satisfactorily.
204B	1	Brass plates clamped directly to top of tantalum screen.	Anode immediately became hot at 50 amperes and 0.13 amp./cm.^{2}.
219	1 to 24	Silver and copper sprayed on lead dioxide in successive coats. Current contacts to #10 copper wire embedded in 1/8" thick sprayed copper deposit.	Operated at 100 amperes without local heating. Current density = 0.28 amp./cm^2.
221 to 230	All	Silver and copper sprayed on lead dioxide in successive coats. Copper wire current lead soft soldered to sprayed copper deposit.	Operated at 10 to 15 amperes without local heating. Current density =0.3 amp./cm^2.

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TABLE X

OTHER CURRENT LEADS TO LEAD DIOXIDE ANODES

Electrode No.	Description of Current Lead	Observations
	Lead dioxide on magnetite - current lead (Universal clip).	Anode became hot (about 100°C.) at current contact lead to magnetite.
191A	Lead dioxide on copper sheet backed with glass plate	Copper sheet dissolved in acid lead nitrate plating bath (Formula LN-2).
191D	Lead dioxide on Monel sheet.	Monel sheet dissolved in acid lead nitrate plating bath (Formula LN-2).
197A	18 B&S copper wire tightly wound around tantalum rod with two ends of copper wire as external current leads. Lead dioxide to be plated over tantalum and copper wire.	Copper wire eroded in acid lead nitrate plating bath (Formula LN-2). No lead dioxide deposited.
197B	20 B&S Nickel wire tightly wound around tantalum rod with two ends of nickel wire as external current leads.	Lead dioxide plated on nickel and tantalum. Lead dioxide plate protected nickel wire from erosion
198	Same as for 197B.	Same as for 197B.
204A	18 B&S Nickel wire threaded through tantalum screen and twelve strands brought up through two 1/4" nickel tubes slotted 1-1/2" to slide on tantalum screen. Nickel wire and tube to serve as current leads.	Nickel wire and nickel tubing dissolved in acid lead nitrate plating bath (Formula LN-2) at plating bath level.
204B	20 B&S nickel wire threaded through tantalum screen-ten strands to serve as external current leads.	Nickel wire dissolved in acid lead nitrate plating bath (Formula LN-2).

Continued

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TABLE X. (cont.) (2)

Electrode No.	Description of Current Lead	Observations
206A, 206B	As for 204B, except 22 of #16 B&S nickel wires sandwiched between folded tantalum screen for 2" at top prior to PbO_2 deposition.	Incomplete PbO_2 coverage on tantalum near area of nickel wires.
208	As for 204, except 16 B&S nickel wires woven into top 3" of tantalum screen. For PbO_2 plating, current contact made only to tantalum.	Complete PbO_2 coverage; nodules formed at edges and along top.
210	Similar to 208, except only top portion of tantalum screen with nickel wires plated first. Other end then plated with 4" overlap on first PbO_2 deposit.	Some erosion of nickel wires.
218	Tantalum screen 3" x 18" plated with PbO_2. As for 208, current contact made to tantalum for plating.	Some nickel wires completely eroded in plating bath.
	Thin spray coatings of zinc, lead, copper, tin, silver and aluminum on 1/4 inch diameter PbO_2 rods. "Metco" wire spray gun used.	Only silver over PbO_2 gave low voltage drop contact. Silver over PbO_2 - .002 volts All others - 0.5-1.5 volts (current = 0.5 ampere)
	Repeat of above, with care taken to avoid heating lead dioxide much above 100°C.	Metal to PbO_2 potential drops (current = 1 ampere). Silver over PbO_2 - .0002 volt. All others - about 0.15 volt.
	Repeat of above, but using Colmonoy Sprayweld Process, the feed for which is powdered metal instead of wire.	Metal to PbO_2 potential drops (current = 1 ampere). Silver over PbO_2 - .0002 volt. All others - 0.6-1.5 volt. except copper over PbO_2 - 0.03 volt.
	Silver deposited on lead dioxide by chemical reduction.	Metal to PbO_2 potential drops (current = 1 ampere). Silver over PbO_2 - .0004 volt.

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TABLE XI

SPECIFIC RESISTANCE AT ROOM TEMPERATURE OF VARIOUS SAMPLES OF LEAD DIOXIDE COMPARED WITH OTHER MATERIALS

Description of Sample	Specific Resistance Ohm-cm. x 10^{-6}	
	Porous	Dense
Lead dioxide		
Storage battery positive active material, 46% porosity (3)	7,400	
Pressed powder, 32% porosity (3)	14,200	
Electrolyzed from lead perchlorate (3)		94 to 405
Electrolyzed from lead sulfamate (3)		1,200
Electrolyzed from dilute lead nitrate solution (4)		92 to 97
Electrolyzed from acid lead nitrate bath (Formula LN2) at Pennsalt (5)		40 to 50
Other Materials		
Graphite	800	
Mercury	96	
Bismuth	115	
Platinum	10.5	
Copper	1.69	
Silver	1.62	

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TABLE XII

MISCELLANEOUS ANODE MATERIALS (BEARING MATERIALS - CARBON IMPREGNATED WITH VARIOUS METALS)
ELECTROLYTE - 600 g/l $NaClO_3$

Research Notebook Reference	Description of Sample and Source	Specific Resistance x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)
1364:186	From the Carbone Corp., Boonton, N.J. RSS - Copper	667	1.5	100	3-4	12	Blue-black precipitate in electrolyte and anode sample appreciably eroded.
1364:187	RS - Copper	167	1.5	100	4.0	12	Blue-black precipitate in electrolyte and anode sample appreciably eroded.
1364:188	RSS Babbitt	855	1.5	100	4.0	12	Brown precipitate in electrolyte and anode sample appreciably eroded.
1364:189	RS Babbitt	480	1.5	100	4.0	12	Brown precipitate in electrolyte and anode sample appreciably eroded.
1364:190	RS Silver	400	1.5	100	4.0	12	Cloudy electrolyte; anode sample etched; least erosion of all bearing material samples.

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TABLE XXII

ELECTRICAL CONDUCTIVITY RATING OF SOME MINERALS*

Conductivity rating: Nonconductor -; very poor conductor +; poor conductor ++; good conductor +++; excellent conductor ++++.

Mineral	Composition	Conductivity Rating
Stibnite	Sb_2S_3	-
Bismuthinite	Bi_2S_3	+++
Kermesite	Sb_2S_2O	+++
Pyrite	FeS_2	++++
Cobaltite	CoAsS	+++
Gersdorffite	NiAsS	++
Ullmannite	NiSbS	+++
Loellingite	$FeAs_2$	+++
Safflorite	$(Co,Fe)As_2$	+++
Rammelsbergite	$NiAs_2$	+++
Marcasite	FeS_2	+++
Arsenopyrite	FeAsS	+++
Glaucodote	(Co,Fe)AsS	++
Molybdenite	MoS	++
Krennerite	$AuTe_2$	++
Sylvanite	$AgAuTe_2$	++
Skutterudite	$(CoNi)As_3$	++
Smaltite Bismuthian	$(CoNi)As_{3-x}$	++
Chloanthite	$(NiCo)As_{3-x}$	++
Pyrargyrite	Ag_3SbS_3	++
Proustite	Ag_3AsS_3	++
Xanthoconite	$AgAsS_3$	++
Wittichenite	Cu_3BiS_3	+++
Tetrahedrite	$(CuFe)_{12}\ Sb_4S_{13}$	++
Pyrochroite	$Mn(OH)_2$	-
Manganite - pseudo Calcite	$Mn_2O_3 \cdot H_2O$	+++
Psilomelane	$BaMn_2 \cdot Mn_8O_{16}(OH)_{14}$	++++
Goethite	$Fe_2O_3 \cdot H_2O$	-
Limonite	$Fe_2O_3 \cdot 3H_2O$	-
Magnetite - Isometric N.Y.	Fe_3O_4	++++
Cassiterite	SnO_2	+
Pyrolusite	MnO_2	+++
Rutile	TiO_2	-
Braunite	$(MnSi)_2O_3$	-
Valentinite - Canada	Sb_2O_3	++
Arsenolite	As_2O_3	++
Ilmenite	$FeTiO_3$	+
Hematite - Specular	Fe_2O_3	+

*The conductivity varied greatly in different specimens of the same mineral species.

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TABLE XIII - Cont.

Hematite - Rhombohedral Michigan	Fe_2O_3	++++
Corundum	Al_2O_3	-
Zincite	ZnO	+
Cuprite - Isometric	Cu_2O	+++
Jamesonite	$2PbS \cdot Sb_2S_3$	-
Cosalite	$Pb_2Bi_2S_5$	++++
Aikinite	$PbCuBiS_3$	++
Bournonite	$PbCuSbS_3$	++
Enargite	Cu_3AsS_4	++++
Famatinite	Cu_3SbS_4	+++
Tennantite	$(Cu,Fe)_{12}As_4S_{13}$	+++
Franklinite	$ZnFe_2O_4$	++
Chromite	$FeCr_2O_4$	+
Cerargyrite	AgCl	+
Tetradymite	Bi_2Te_2S	+++
Nagyagite	$Pb_5Au(TeSb)_4S_5$	++++
Domeykite	Cu_3As	+++
Algodonite	Cu_6As	+++
Dyscrasite	Ag_3Sb	++++
Argentite	Ag_2S	+++
Hessite	Ag_2Te	++
Berzelianite	Cu_2Se	++
Petzite	Ag_3AuTe_2	+++
Chalcocite	Cu_2S	++++
Stromeyerite	CuAgS	+++
Bornite	Cu_5FeS_4	+++
Galena	PbS	++++
Clausthalite	Pb-CuSe	++
Altaite	PbTe	+++
Sphalerite - Ferriferous	ZnS	++
Metacinnabar	HgS	++++
Tiemannite	HgSe	++++
Chalcopyrite	$CuFeS_2$	++++
Stannite	Cu_2FeSnS_4	+++
Pyrrhotite	$Fe_{1-x}S$	++++
Niccolite	NiAs	+++
Millerite	NiS	++++
Pentlandite	$(FeNi)_4S_8$	+++
Cubanite	$CuFe_2S_3$	+++
Covellite	CuS	+++
Sternbergite	$AgFe_2S_3$	-
Cinnabar	HgS	-
Tetrahedrite - Mercurian	$(CuFe)_{12}Sb_4S_{13}$	+++
Siegenite	$(CoNi)_3S_4$	+++
Carrollite	Co_2CuS_4	++

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TABLE XIV

MINERALS TESTED

RESEARCH NOTEBOOK REFERENCE	DESCRIPTION OF SAMPLE *	AVERAGE CELL CURRENT (AMPS.)	ANODE CURRENT DENSITY (APPROX) MA./SQ.CM	AVERAGE CELL VOLTAGE	CELL TEMP. °C.	RESULT (ANODE)
1449-17	Cassiterite from England	0.73	100	20-38	25-40	Erosion with orange-yellow ppt. appearing in electrolyte. Exploding cell. Current contact hot.
1449-17	Cassiterite from South Dakota	0.9	100	14-19	25-35	Erosion with orange ppt. appearing in electrolyte. Current contact hot.
1449-18	Psilomelane (Orthorhombic)	1.6	100	20	25	High contact resistance.
1449-18	Psilomelane (Massive)	2.6	100	11	25	Erosion with gray ppt. appearing in electrolyte Current contact hot.
1449-18	Ilmenite	4.5	100	12-15	25-45	High contact resistance
1449-19	Hematite	0.1	100	44	25	Cell operated at impractical high voltage.
1449-19	Pyrolusite	0.5-1.5	100	6.6-20.0	25-28	Cell operated at increasingly high voltage. Sample was not uniformly pyrolusite and current distribution from contact was poor.
1449-19	Zincite	1.1	100	40	25	Cell operated at impractical high voltage

* All mineral samples were obtained from Ward's Natural Science Est.

TABLE XV

MISCELLANEOUS ANODE MATERIALS

Research Notebook Reference	Description of Sample and Source	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)
1400:14	Silicon ferrite from Horisons, Inc.	5.0	294	4.2-5.0	11	Appreciable erosion of anode sample as evidenced by dark red-brown electrolyte
1400:15	Impervious graphite from Falls Industries	5.0	149	5.0-5.3	11	Appreciable erosion of anode sample as evidenced by black electrolyte
1400:16	Manganite from Penn State College	2.0	125	11-12	11	No noticeable erosion
1400:16	Natural graphite from Ward's Natural Science Establishment	10.0	200	6.0	-	Very rapid erosion
1400:57,93	Nickel-ferrite boule from Linde Air Products Co.	1.2	200	7.0-8.6	12	No noticeable erosion but conversion of chlorate to perchlorate was very low
1400:56	Gold Rod	1.0	100	4.0	5	Anode weight loss was 43 mg. per ampere hour; orange precipitate formed in electrolyte and a rust colored film formed on gold rod.
1364:177	Silver Sheet	2.6	200	6.1-19.0	0-2	Electrolyte was maintained alkaline at a pH from 7.5 to 8.5. Silver surface is etched unevenly and also a dark gray smut is formed. Appreciable erosion even after silver sample was first anodically electrolyzed in 15% sodium hydroxide to form a black deposit.
1449-120	Electrolytic Manganese	2.7	190	1.7-4.3	20-26	Almost all of sample eroded away after 2 hours of electrolysis. Some explosions observed.

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TABLE XVI

PITTSBURGH PLATE GLASS SAMPLES

Research Notebook Reference	Description of Sample	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)
1400:47,61	Tin Oxide Block-Sample A123-NESA on the large unsilvered faces.	1.0-2.3	50-200	5.1-9.8	12	Slight amount of pinpoint erosion. Cell operated at about 15% current efficiency.
1400:17,71	Tin Oxide Block-Sample B92-NESA on the large unsilvered face.	0.96	100	20-44	12	Poor conductor so that good electrical contact could not be obtained.
1400:59	Tin Oxide Block-Sample B6- No NESA coating on any face.	1.0	200	6.2-14.0	12	No noticeable erosion. Cell operated at about 17% current efficiency.
1400:58	Tin Oxide Block-Sample B53-No NESA coating on any face.	1.0	115	4.2-7.5	12	No noticeable erosion. Cell operated at about 50% current efficiency.
1400:72	Polished Plate Glass-NESA Solution "A" on one face (4 samples).	0.5-1.8	-	60-110	-	All these samples operated at very low current and high voltage with either the conductive film coming off as a cloud, or the plate glass cracking at the electrolyte level, or the current lead melting off because of the heat generated.
1400:72	Polished Plate Glass-NESA Solution "B" used for coating the faces (4 samples).	0.5-1.8	-	60-110	-	

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TABLE XVII

CORNING GLASS WORKS SAMPLES

Research Notebook Reference	Description of Sample	Average Cell Current (Amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)
1400:48,60	Sample A - Conducting Refractory	2.6	200	7.8-9.0	12	Appreciable erosion giving electrolyte white cloudy appearance. Current efficiency was about 40%.
1400:50	Sample B - Conducting low expansion glass	0.6	-	43	-	Operated at too high cell voltage to be considered practical.
1400:49	Sample C - E.C.Glass Rod	2.6	245	6.0-33	12	Appreciable erosion giving electrolyte a white cloudy appearance.

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TABLE XVIII

PRESSED LEAD DIOXIDE-MANGANESE DIOXIDE-MAGNETITE MIXTURES

SAMPLE NUMBER	COMPOSITION OF MIXTURE BEFORE FIRING WEIGHT PERCENT					FIRING CONDITIONS	SCREENING TESTS OF FIRED SAMPLE			
				BINDER			ELECTRICAL CONDUCTIVITY	POROSITY	HARDNESS	STABILITY IN SATURATED SODIUM CHLORATE SOLUTION
	PbO_2	MnO_2	Fe_3O_4	50% KOH	38° BAUMÉ KOH SOD. SIL. SOLN.					
5-1	97.53			2.47		Dried 16.5 hrs. in air at 190°C.; then fired 3 hrs. in O_2 at 300°C.	Good	Fair	Fair	
5-2	95.25			4.75		Ditto	Good	Fair	Good	Disintegrated
5-3	95.25			4.75		Ditto	Good	Poor	Good	- - - -
5-7	95.28				4.72	Ditto	Good	Poor	Fair	- - - -
5-8	93.08				6.92	Ditto	Good	Poor	Fair	- - - -
5-9	95.28				4.72	Ditto	Good	Fair	Good	Fair
6-1	71.6	24.2		4.2		Fired 3 hrs. in O_2 at 300°C.	Good	Poor	Good	Poor
6-2	47.8	47.8		4.2		Ditto	Fair	Poor	Good	- - - -
6-3	24.2	71.6		4.2		Ditto	Fair	Poor	Poor	- - - -
6-4	70.6	23.8			5.6	Ditto	Fair	Fair	Fair	- - - -
6-5	47.2	47.2			5.6	Ditto	Poor	Poor	Fair	- - - -
6-6	23.8	70.6			5.6	Ditto	Poor	Poor	Poor	- - - -
8-1	71.2	24.0		4.8		Dried 16.5 hrs. in air at 190°C.	Good	- -	- -	Poor
9-1	47.2	47.2			5.6	Dried 16.5 hrs. in air at 180°C.	Poor	Poor	Poor	- - - -
9-2	47.2	47.2			5.6	Ditto	Poor	Fair	Fair	- - - -
10-1	71.6	24.2		4.2		Fired 3 hrs. in air at 300°C.	Good	Poor	Good	Poor
10-2	47.8	47.8		4.2		Ditto	Fair	Poor	Good	- - - -
10-3	24.2	71.6		4.2		Ditto	Poor	Poor	Poor	- - - -
10-4	70.6	23.8			5.6	Ditto	Good	Fair	Fair	Fair
10-5	47.2	47.2			5.6	Ditto	Fair	Poor	Fair	- - - -
10-6	23.8	70.6			5.6	Ditto	Poor	Poor	Poor	- - - -
10-7	71.6		24.2	4.2		Ditto	Good	Poor	Good	Good

(Continued)

TABLE XVIII. (cont.) (2)

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SAMPLE NUMBER	COMPOSITION OF MIXTURE BEFORE FIRING WEIGHT PERCENT					FIRING CONDITIONS	SCREENING TESTS OF FIRED SAMPLE			
				BINDER			ELECTRICAL CONDUCTIVITY	POROSITY	HARDNESS	STABILITY IN SATURATED SODIUM CHLORATE SOLUTION
	PbO_2	MnO_2	Fe_3O_4	50% KOH	38°BAUME KOH SOD.SIL.SOLN.					
10-8	47.8		47.8	4.2		Fired 3 hrs. in air at 300°C.	Fair	Poor	Good	- - - -
10-9	70.6		23.8		5.6	Ditto	Good	Good	Good	Good
10-10	47.2		47.2		5.6	Ditto	Fair	Poor	Good	- - - -
11-1	71.6		24.2	4.2		Fired 3 hrs. in O_2 at 300°C.	Good	Poor	Good	Good
11-2	47.8		47.8	4.2		Fired 3 hrs. in O_2 at 300°C.	Fair	Fair	Good	- - - -
11-3	70.6		23.8		5.6	Ditto	Good	Fair	Good	Good
11-4	47.2		47.2		5.6	Ditto	Fair	Poor	Good	- - - -
18-1	71.6		24.2	4.2		Fired 6 hrs. in air at 300°C.	Good			
18-2	71.6		24.2	4.2		Fired 18.5 hrs. in air at 300°C.	Fair			
18-3	75		25			Fired 6 hrs. in air at 300°C.	Good			
18-4	75		25			Fired 18.5 hrs. in air at 300°C.	Good			
18-5	71.6		24.2	4.2		Fired 6 hrs. in air at 300°C.	Good			Good
18-6	71.6		24.2	4.2		Ditto	Good	TESTED IN CHLORATE-PER		CHLORATE CELL
18-7	71.6		24.2	4.2		Fired 18.5 hrs. in air at 300°C.	Good			Good
18-8	71.6		24.2	4.2		Ditto	Good	TESTED IN CHLORATE-PER		CHLORATE CELL

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TABLE XVIII. (cont.) (3)

NOTES:

Electrical Conductivity (Qualitative)
Good - 100 Ohm or less
Fair - 100 Ohm to 500 Ohm
Poor - Greater than 500 Ohm

Porosity
Good - More than ten seconds elapsed before ink drop was absorbed.
Fair - Several seconds elapsed before ink drop was absorbed.
Poor - Ink drop absorbed immediately.

Hardness - A pointed steel scribe was scratched across surface of sample.
Good - Very small impression on surface.
Fair - A shallow impression made.
Poor - Removed a quantity of material without much effort.

Stability in Saturated Sodium Chlorate Solution
Good - Sample maintained its shape and nearly all its bulk although a comparatively small amount of powder spread through the saturated sodium chlorate solution.
Fair - Sample did not break up completely although a large amount of powder was lost.
Poor - Sample disintegrated.

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TABLE XIX

CHROMIUM BORIDE SAMPLES (BOROLITE III A) FROM
ELECTRO METAL CORPORATION

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RESEARCH NOTEBOOK REFERENCE	DESCRIPTION OF SAMPLE	AVERAGE CELL CURRENT (AMPERES)	ANODE CURRENT DENSITY (APPROX.) MA./SQ.CM.	AVERAGE CELL VOLTAGE	CELL TEMP. °C.	RESULT ANODE
1449-23	Borolite III A Sample 2	1.4	100	3.2 - 3.6	25	Erosion of anode with electrolyte turning dark brown in 5-1/2 hrs
1449-24	Sample 4	1.4	100	3.2 - 3.4	25	Erosion of anode with electrolyte turning dark brown in 5-1/2 hrs
1449-25	Sample 6	1.4	100	3.2 - 3.4	25	Erosion of anode with electrolyte turning dark brown in 5-1/2 hrs

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TABLE XX

Platinum-Palladium Alloys

ANODE SAMPLE	APPROXIMATE EROSION LOSS MILLIGRAMS PER AMPERE - HOUR	REMARKS
100% Platinum	The erosion rates of these materials were too small to measure accurately during a short period of operation.	
95% Platinum 5% Palladium		
90% Platinum 10% Palladium		
80% Platinum 20% Palladium (Sample 1)	0.006	Electrolyte turned light orange after one hour of operation.
80% Platinum 20% Palladium (Sample 2)	0.006 to 0.01	Current efficiency was from 83 to 87%.
60% Platinum 40% Palladium	0.8	Current efficiency was about 50% and electrolyte turned orange color in about 3 hours of electrolysis.
100% Palladium	5.2	Electrolyte turned black after one hour of operation.

Anode current density - 300 ma./sq.cm.

Temperature - about 20°C.

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TABLE XXI

PLATINUM-RUTHENIUM ALLOYS

ANODE SAMPLE	APPROXIMATE EROSION LOSS MILLIGRAMS PER AMPERE-HOUR	REMARKS
100% Platinum	Too small an erosion rate to measure accurately during a short period of operation.	
88% Platinum - 12% Ruthenium	0.002 to 0.005 to about 10°C. 0.03 at about 45°C.	Electrolyte became light tan color at higher temperature.
100% Ruthenium	27.2	Electrolyte turned orange-yellow after 5.75 hours of operation. Anode sample turned black.

Anode current density - 300 ma./sq.cm.
Temperature - about 20°C. except where noted.

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TABLE XXII

PALLADIUM-RUTHENIUM ALLOYS

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ANODE SAMPLE	APPROXIMATE EROSION LOSS MILLIGRAMS PER AMPERE-HOUR	REMARKS
100% Palladium	5.2	Electrolyte turned black after one hour of operation.
88% Palladium 12% Ruthenium	4.0	Electrolyte turned brown after one hour of operation. Sample colored reddish-brown.
100% Ruthenium	27.2	Electrolyte turned orange after two hours of operation.

Anode current density - 300 ma./sq.cm.
Temperature - about 20°C.

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TABLE XXIII
COLD PRESSED AND SINTERED Si - SiC SERIES
CATEGORY NO. 1

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm. x10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Fired 2 hrs. at 1350°C. in atmosphere of carbon monoxide:-							
100% Silicon (200 MXD)	1-17	543,000	1.95	100	6.6-28	11-27	No noticeable attack on anode at end of 9.5 hrs. electrolysis. Increase in cell voltage from 6.6 - 28 v during this period.
100% Silicon (200 MXD)	1-19	1,178,000	4	200	24-36	- -	Cell operation stopped after 6 min. because of high cell voltage.
100% Silicon	1-25	- -	4	200	20-35	12	No erosion. Increase in cell voltage from 20-35 v in 18 min. Operation stopped because of high cell voltage.
50% silicon (200 MXD); 50% silicon (30 grit)	1-18	295,000	2.2	100	6.3-24.0	11-15	No appreciable erosion over 4 hr. period. Cell voltage increased from 6.3v to 24.0 v during this time.
50% Si (200 MXD) 50% Si (30 grit)	1-24	135,800	4	200	- -	- -	Sample became red hot at portion above electrolyte after about 1 minute of operation.
95% Si (200 MXD) 5% SiC (100 grit)	1-26	756,000	3.7(47min) 1.8(12hrs 32 min)	200 100	11-31.5	12-20	Stopped when cell voltage reached 31.5 volts after 13.3 hours of operation. No explosions and no erosion.
90% Si (200 MXD) 10% SiC (100 grit)	1-27	574,000	3.7(53min) 1.8(12hrs 32 min)	200 100	11-30	12-20	Stopped when cell voltage reached 30 v after 13.5 hrs. operation. A few very small explosions caused small pieces to come from anode surface.

(Continued)

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TABLE XXIII (cont.) (2)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm. x10^{-6}	Average cell Current (amperes)	Anode Current Density (approx) ma/sq cm	Average cell Voltage	Cell Temp °C	Effect on Anode
90% Si (200 MXD) 10% SiC (100 grit)	1-16	475,000	2.0	100	7-27.5	11	Very little erosion at surface level of electrolyte. Increase in cell voltage from 7 to 27.5 volts over 4.5 hour period.
90% Si (200 MXD) 10% SiC (100 grit)	1-23	690,000	4	200	14-35	14-30	Small amount of erosion at electrolyte surface. Cell voltage increased from 14 to 35 volts in 3.75 hours. No explosions.
85% Si (200 MXD) 15% SiC (100 grit)	1-28	705,000	3.7(53min) 1.8(8 hrs 10 min)	200 100	11-32	12-20	Stopped when cell voltage reachsd 32v after 9 hrs. Few very small explosions caused small pieces to come from anode surface.
80% Si (200 MXD) 20% SiC (100 grit)	1-29	378,000	3.7(53min) 1.8(2 hrs 55 min)	200 100	14-35	12-25	Operation of cell stopped when cell voltage reached 35v with anode current density of 100 ma/sq.cm. after 3.8 hrs. A few very small explosions caused small pieces to come from anode surface.
75% silicon (200 MXD) 25% SiC (100 grit)	1-15	595,00	2.2	100	8.0-19.5	11-15	No appreciable erosion over 4 hr. period. Contact heated up which finally caused plastic cell cover to catch fire.
75% Si(200 MXD) 25% SiC (100 SGM)	1-20	753,000	4	200	18-35	14-46	Small amount of erosion at electrolyte surface. Cell voltage increased from 18 - 35 v in 4 hours. No explosions
75% Si 25% SiC (100 SGM)	1-30	- -	4	200	12-30	12	No appreciable erosion. Slight attack at electrolyte level. Increase in cell voltage from 12-30v in 3.5 hrs. Faint Explosions from cell.
50% Si (200 MXD 50% SiC (100 grit)	1-14	810,000	2.0	100	9-25	11	Anode ran hot with very slight erosion at surface level of electrolyte. Increase of cell voltage from 9v to 25v over 6 hour period of electrolysis.

(Continued)

TABLE XXIII (cont.) (3)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm. x10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C	Effect on Anode
50% Si (200 MXD) 50% SiC (100 SGM)	1-21	575,000	4	200	16-38	16	Cell voltage increased from 16 to 38 v in 2.5 hours. Anode lead became very hot. No erosion and no explosions.
25% Si (200 MXD) 75% SiC (100 grit)	1-13	893,000	2.0	100	11-27	11	No appreciable erosion over one hour period but cell voltage increased from 11 v to 27 v.
25% Si (200 MXD) 75% SiC (100 SMG)	1-22	654,000	4	200	16-35	16-30	Cell voltage increased from 16 to 35 volts in 20 minutes. Anode current lead became very hot. No erosion and no explosions.
Sintered at 1350°C for 2 hours in a helium atmosphere:- 100% silicon (200 MXD)	1-5	27,800	2.0	100	7-40	11-12	Very little erosion. Slow polarization (increase in cell voltage from 7-40 v over 5 hour period.
100% silicon (200 MXD)	1-7	879,000	4	200	15-36	26-36	No erosion. Increase in cell voltage from 15-36 v in 0.75 hr. Several cracks in portion of anode immersed in electrolyte at end of test.
50% silicon (200 MXD) 50% silicon (30 grit)	1-6	242,000	1.95	100	5.8-50	11	Increase in cell voltage from 5.8-50 v over 3 hrs. No noticeable erosion.
95% Si (200 MXD) 5% SiC (100 SGM)	1-8	80,400	4	200	8.0-35.0	36-30	No explosions and no erosion. Increase in cell voltage from 8.0-35.0v in one hour.
90% Si - 10% SiC	1-4	- -	4	200	14-20	18-43	Electrolyte drawn up within anode by wick action and reacts with anode clamp. Anode clamp area becomes hot. No appreciable attack on anode in 2 hours.
90% Si (200 MXD) 10% SiC (100 SGM)	1-9	90,500	4	200	9.0-39.0	20-43	No explosions and no erosion. Increase in cell voltage from 9.0-39.0v in one hour. When washed with tap water after run, anode mechanically disintegrated into layers.

(Continued)

TABLE XXIII (cont.) (4)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
85% Si (200 MXD) 15% SiC (100 SGM)	1-10	110,500	4	200	7.8-26.0	20-43	No explosions. Increase in cell voltage from 7.8 - 26 v in one hour. Mechanical disintegration of anode in layers. Electrolyte black.
80% Si (200 MXD) 20% SiC (100 grit)	1-11	60,500	1.8	100	4-35	12	No explosions and no erosion. Cell operation stopped when cell voltage reached 35v after 3.5 hours.
75% Si - 25% SiC	1-3	- -	4.6	200	23-26	35-30	Anode becomes hot at current lead clamp. Electrolyte drawn up within anode by wick action and attacks anode clamp.
75% Si (200 MXD) 24% SiC (100 SGM)	1-12	226,000	4	200	7.8-36.0	2-33	No noticeable erosion. Increase in cell voltage from 7.8 - 26.0 v in 0.83 hr. No explosions.
50% Si - 50% SiC	1-2	- -	4	200	26-35	25-30	Anode becomes hot at current lead clamp; electrolyte drawn up within anode by wick action & attack anode clamp.
25% Si - 27% SiC	1-1	- -	0.2	25	25	18	Surface erosion advanced after only 5 min. electrolysis. Electrode soaking for one hour before current was applied.
Cold pressed and sintered at 1350°C. for 2 hours in purified CO:- 72% Si (200 MXD) 8% SiC(100 grit SGM) 20% MnO_2	1-31	164,000	2.64	125	5.2-30	-	Appreciable erosion particularly at electrolyte level. The outer walls came off in sheets, leaving the immersed area very rough with large pin holes. Increase in cell voltage from 5.2v to 30v after 8.75 hours operation.
80% Beta silicon carbide 14% Silicon (200 MXD) 6% Carbon, cold pressed and sintered at 1350°C for 2 hours in purified CO atmosphere.	1-33	178,000	2	98	4.7-8.0	12	Extremely heavy erosion, particularly at electrolyte level; bottom portion dropped off after 22 minutes of operation. No explosions.

(Continued)

TABLE XXIII (cont.) (5)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm X10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Cold pressed and sintered at 1350°C. for 2 hrs. in purified CO:- 85.5% Si (200 MXD) 9.5% SiC (100 SGM) 5.0% CaF_2	1-35	16,000,000	3.2	150	45	12	Operated at impractical high cell voltage. Anode became very hot and contact smoked.
Cold pressed and sintered at 1350°C. for 2 hrs. in purified CO:- 85% Beta SiC (40 & F) 15% Si (200 MXD)	1-34	306,000	3.2	150	13-26	12	Slight erosion observed. Anode sample became so hot that plastic cell lid caught fire. Cell voltage increased from 13-26 V. in 10 min.
Cold pressed and sintered at 1350°C. for 2 hrs. in CO:- 85.5% Si (200 MXD) 9.5% SiC (100 SGM) 5.0% Fe_3O_4	1-36	1,180,000	2.2	100	10-30.5	12	Slight erosion at electrolyte level with reddish-brown ppt. forming in electrolyte. Increase in all voltage from 10 to 30.5 volts in 7 hours. No explosions.
72% Si (200 MXD) 8.0% SiC (100 SGM) 20.0% Fe_3O_4	1-37	1,200,000	2.2	100	11-30.0	12	Slight erosion at electrolyte level with reddish-brown ppt. forming in electrolyte (more ppt. than with sample No. 1-36). Increase in cell voltage from 11-30 V. in 2 hours. No explosions.
85.5% Si (200 MXD) 9.5% SiC (100 SGM) 5.0% Pb	1-38	831,000	2.2	100	8.2-30.0	12	No noticeable erosion with electrolyte remaining practically clear after 9 hrs. of operation. Increase in cell voltage from 8.2 to 30.0 V. during this period.

(Continued)

TABLE XXIII (cont.) (6)

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Description of Anode Material	Sample No.	Specific Resistivity ohm-cm $X10^{-6}$	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp. °C.	Effect on Anode
72% Si (200 MXD) 8.0% SiC (100 SGM) 20% Pb	1-39	687,000	2.2	100	7.6-30.0	12	No noticeable erosion with electrolyte remaining practically clear after 8.5 hrs. of operation. Increase in cell voltage from 7.6 to 30.0 V. during this period
85.5% Si (200 MXD) 9.5% SiC (100 SGM) 5.0% $FeO \cdot TiO_2$	1-40	1,518,000	2.2	100	13-40	12	Considerable erosion with reddish-brown ppt. and particles of anode in electrolyte after 8.5 hrs. of operation. Increase in cell voltage from 13 to 40 V. during this period.
72% Si (200 MXD) 8.0% SiC (100 SGM) 20% $FeO \cdot TiO_2$	1-41	769,000	2.2	100	6.9-18.0	12	Operated for about 16 hours with considerable erosion over all of immersed area with failure caused by anode breaking off at electrolyte level.
85.5% Si (200 MXD), 9.5% SiC (100 SGM), 5.0% TaC (200 mesh), cold pressed and sintered at 1350°C. for 2 hours in CO atmosphere.	1-42	4,600,000	3.0	146	11-30	27-43	Very slight erosion at electrolyte level with cell voltage increasing from 11 to 30 volts after 1.75 hours of operation.
72.0% Si (200 MXD), 8.0% SiC (100 SGM), 20% TaC (200 mesh), cold pressed and sintered at 1350°C. for 2 hrs. in CO atmosphere.	1-43	3,800,000	3.0	146	11-30	27-42	Very slight erosion at electrolyte level with cell voltage increasing from 11 to 30 V. after 2.5 hrs. of operation.

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TABLE XXIV
SILICON ALLOY IMPREGNATION
CATEGORY NO. 2

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Cast stock impregnated with purified silicon	2-1	32,400	1.95	100	4.6-8.6	11	Exploding anode which finally blew in two. Very slight erosion noticed over 1.3 hr. period.
Cast stock impregnated with low calcium silicon	2-2	26,800	0.8-2.0	100	4.6-20.0	11	Exploding anode. Anode slightly attacked by explosions with some erosion material present in electrolyte.
Cast stock impregnated with low aluminum silicon	2-3	45,100	1.95	100	4.6-18.0	11	Crackling anode with finally a very loud explosion blowing anode sample [illegible]. Some noticeable erosion.
Extruded stock impregnated with silicon containing: 3% sodium chlorate	2-4	4,070	4	200	5.2-8.4	15-16	Exploding anode. About 1/4 of anode eroded away in 3 hrs. Electrolyte black.
5% sodium chlorate	2-5	4,490	4	200	5.6-9.6	15-16	Exploding anode. About 3/8 of anode eroded away in 3 hrs. Electrolyte black.
10% sodium chlorate	2-6	6,780	4	200	5.4-7.8	15-16	Exploding anode. About 1/2 of anode eroded away in 3 hrs. Electrolyte black.
20% sodium chlorate	2-7	4,530	4	200	5.5-7.8	15-16	Exploding anode. About 1/2 of anode eroded away in 3 hrs. Electrolyte black.
3% lead	2-8	5,430	4	200	5.6-12.0	15-16	Exploding anode; broke beaker after 1 hr. operation. Mainly anode blew off 3/4" below electrolyte level. Electrolyte black.
5% lead	2-9	4,110	4	200	5.4-8.2	15-16	Exploding anode. About 3/8 of anode eroded away in 3 hrs. Electrolyte black.
10% lead	2-10	5,430	4	200	5.6-8.0	12	Exploding anode. About 1/2 of anode eroded away in 2.75 hrs. Electrolyte black.

(Continued)

TABLE XXIV, (cont.) (2)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C	Effect on Anode
20% lead	2-11	3,810	4	200	5.6-9.1	12	Exploding anode. About 1/2 of anode eroded away in 2 hrs; an explosion broke cell beaker at end of period. Electrolyte black. With this, cell voltage immediately dropped and then gradually increased.
Extruded stock impregnated with silicon containing 5% lead dioxide	2-12	3,770	2	100	3.8-6.6	12	Appreciable anode erosion; anode exploded, finally breaking sample in half just below electrolyte level; electrolyte black from anode erosion.
Extruded stock impregnated with silicon containing 20% lead dioxide	2-13	3,570	2	100	3.9-7.3	12	Same as sample above (No. 2-12) with final failure caused by a loud explosion which broke anode in half.
Extruded stock impregnated with silicon containing 5% tungsten	2-14	3,570	2	96	4.0-6.8	12	Same as sample above (no. 2-12) with final failure caused by a loud explosion which broke anode in half.
Extruded stock impregnated with silicon containing 20% tungsten	2-15	2,310	2	105	3.8-8.1	12	Same as sample above (no. 2-12) with final failure caused by a loud explosion which broke anode in half.
Extruded stock impregnated with silicon containing 5% $MoSi_2$	2-16	2,930	2	98	3.8-7.8	12	Appreciable anode erosion but with only one final explosion which broke anode inhalf after 3 hours.
Extruded stock impregnated with silicon containing 20% $MoSi_2$	2-17	2,310	2	100	3.9-8.0	12	Appreciable anode erosion; final explosion shattered glass cell and anode sample.

(Continued)

TABLE XXIV. (cont.) (3)

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Description of Anode Material	Sample No.	Specific Resistivity ohm-cm 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp. °C.	Effect on Anode
Calcined extruded material impregnated with Electromet silicon-titanium alloy	2-18	894	3.2	168	4.8-	12	Anode eroded in half at electrolyte level after 23.5 hours of electrolysis.
Calcined extruded material impregnated with Electromet 35-40% zirconium alloy	2-19	5,320	3.2	157	4.8-6.2	12	Anode eroded in half at electrolyte level after 19.5 hours of electrolysis.
Black extruded stock impregnated with 85% Si + 15% Mn	2-20	39,100	3.6	174	4.8-7.0	12	Cell operated at low voltage with some noticeable erosion for 8 hours. Failure was caused by the anode exploding in half at the electrolyte level.
Durhy extruded material impregnated with 95% Si and 5% Fe	2-21	3,630	3.1	192	4.6-7.3	12	Some erosion with many explosions until failure was caused by sample blowing in two at electrolyte level after 4.6 hours of operation. Explosions started after 2.75 hrs. of operation.
Durhy extruded material impregnated with 80% Si and 20% Fe	2-22	3,640	3.1	200	4.6-6.9	12	Some erosion with many explosions until failure was caused by sample blowing in two at electrolyte level after 7.25 hrs. of operation. Explosions started after 6.25 hrs. of operation.
Durhy extruded material impregnated with 95% Si and 5% magnetite	2-23	3,660	3.1	188	3.7-7.6	12	Some erosion with many explosions until failure was caused by sample blowing in two at electrolyte level after 6.0 hrs. of operation. Explosions started after 3.25 hrs. of operation.

(Continued)

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TABLE XXIV. (cont.) (4)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp. °C.	Effect on Anode
Durhy extruded material impregnated with 80% Si and 20% magnetite	2-24	3,370	3.1	200	4.2-7.0	12	Some erosion with many explosions until failure was caused by sample blowing in two at electrolyte level and breaking cell beaker after 6.5 hrs. operation. Explosions started after 4.25 hrs. of operation.
Durhy extruded material impregnated with 95% Si and 5% ilmenite	2-25	4,750	3.1	200	4.6-7.8	12	Failure caused by anode blowing in two after testing 3 hrs. Some noticeable erosion and many explosions which started after 2.25 hrs. of operation.
Durhy extruded material impregnated with 80% Si and 20% ilmenite	2-26	4,410	3.1	200	4.4	12	Many small explosions with final vigorous one which blew sample in two and broke cell beaker and cooling coil after 4 hrs. of operation. Some noticeable erosion.
Extruded stock impregnated with: 95% silicon containing 5% tantalum carbide	2-27	15,400	3.0	150	4.2-6.4	27-29	Cell operated with many small explosions with final vigorous one which blew sample in half after 7.5 hrs. of operation. Noticeable erosion.
Extruded stock impregnated with: 80% silicon containing 20% tantalum carbide	2-28	15,400	3.0	140	4.6-6.6	27-29	Some noticeable erosion with explosion breaking both anode sample and cell beaker after 3 hrs. of operation.

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TABLE XXV
VARIATIONS IN CARBON BASES
CATEGORY NO. 3

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Durhy - made by siliconizing a carbon body formed by extruding a mixture of wheat flour and carbon powder.	3-1	- -	2.5-5	200	6-9.8	4-15	Severe spalling; end broken off with large pieces in bottom of cell.
Durhy - made by siliconizing a carbon body formed by casting	3-2		0.8-8	200	7-19	5-12	Rlarized; slight spalling.
			0.6-2.8	200	16-19	16-19	Polarized.
Silicon impregnated National Carbon porous carbon #20	3-3	- -	4.5	200	6.5	15	Rapid erosion of anode, - electrolyte becomes black in 1/2 hour.
Silicon impregnated National Carbon porous carbon #30	3-4	- -	4	200	6	21	Rapid erosion of anode, - electrolyte turns black with suspension of fine carbon in 1/2 hour.
Silicon impregnated National Carbon porous carbon #50	3-5	- -	4.6	200	6.4	16	Rapid erosion of anode, - electrolyte becomes black in 1/2 hour.
Silicon impregnated National Carbon porous carbon #60	3-6	- -	4.5	200	7	15	Rapid erosion of anode; electrolyte turns black in 1/2 hour.
Calcined untempered Masonite board, impregnated with silicon	3-7	1,980	2.0	100	5-19	14	No erosion, slow increase in cel voltage from 5-19 v over 6.5 hr. perio
Calcined untempered Masonite impregnated with silicon	3-7	26,000	1.8-2.1	180-186	5.5-23	12-20	Operated 27 hrs. without failure, 30% current efficiency at 16 hrs. No appreciable erosion seen.
Calcined untempered Masonite impregnated with silicon	3-7	22,500	3.0	222	6-21	12	No erosion and no explosions. Ran for 10 hrs. with the voltage going from 6v - 21v. Subsequent treatment with 50% HF did not help.

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TABLE XXV. (cont.) (2)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
National Carbon porous graphite impregnated with silicon in the following grades:-		8,940	4	200	5-11.0	15-30	All of the silicon impregnated porous graphite samples eroded rapidly with no cell explosions. Grade 10 eroded the worst with erosion decreasing from Grade 10 to Grade 60.
Grade 10	3-8						
Grade 20	3-9	3,560	4	200	5-11.0	15-16	See above
Grade 30	3-10	4,850	4	200	5.2-6.4	15-16.5	See Above
Grade40	3-11	5,120	4	200	5.2-6.1	15-16.5	See above
Grade 50	3-12	5,560	4	200	5.0-5.6	15-16	See above
Grade 60	3-13	6,580	4	200	5.0-5.6	15-16	See above
Calcined wood doweling impregnated with silicon	3-15	19,500	1.8	180	20-44	12	Increase in cell voltage from 20-44 v over 1 hr. period. No noticeable erosion. White film over all of immersed area.
Calcined bamboo impregnated with silicon	3-16	23,300	1.8-2.1	205-211	5-10	12	After 18 hrs. operation small shreds of bamboo in bottom of cell. Finally broke off at electrolyte level after 27 hrs. operation. Showed erosion over most of area. About 60% current efficiency.
Calcined bamboo impregnated with silicon	3-16	30,900	2.1	152	2.0-18	12	Operated 27.8 hrs. with gradual increase in cell voltage from 5-18v Erosion, with several small holes appearing at the end of period.

(Continued)

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TABLE XXV, (cont.) (3)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Calcined Homasote impregnated with silicon	3-14	24,600	1.8	111	18-30.3	12	Cell operation stopped when cell voltage reached 30.3v after 9.5 hrs. operation. A few explosions blew off some particles of anode material. No attack at electrolyte level.
Calcined manila rope impregnated with silicon	3-17	30,300	3.0	155	2.0-18.0	12	This sample did not explode or erode. Increase of cell voltage from 5v - 18v over 8 hr. period of electrolysis. Sample failed by breaking off at electrolyte level.
Calcined sa h cord impregnated with silicon	3-18	1,600	0.72	200	5.0-30.0	12	This sample showed signs of erosion all through the electrolysis. Some crackling plus shreds of anode flaking off was noted. Increase in cell voltage from 5v - 30 over 3 hr. period of electrolysis.
Calcined Compreg impregnated with silicon	3-19	33,900	3.0-3.7	121-150	6.4-11	12	After 11 hrs. of electrolysis, the sample cracked at electrolyte level while out of cell overnight. Small chunks were off anode after the 11 hrs. No erosion was noted.
Calcined mailing tube, impregnated with silicon.	3-20	- -	3.0	199	10-32	12	All of immersed area showed signs of eroding. About 6 holes were on the bottom half of sample, from electrolysis. Increase in cell voltage from 10v-32v over 1 hour of electrolysis.
Calcined hardwood charcoal impregnated with silicon	3-21	78,000	2.64	165	13.0-30.5	12	After 0.75 hrs. operation, small explosions started with resulting anode erosion coloring electrolyte black. Cell operated 13 hrs. with increase of cell voltage from 13.0 to 30.5v. Very heavy erosion during last 7.5 hrs.

(Continued)

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TABLE XXV. (cont.) (4)

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Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Effect on Anode
Calcined Walnut Shells impregnated with silicon	3-23	59,300	3.6	200	5.2-22	12	Operated 34 hours with cell voltage leveling off at about 20V. after 10 hrs. Some noticeable erosion.
Calcined untempered Masonite, impregnated with silicon	3-24	41,700	4.5	107	5.8-22	12-28	Operated with no explosions and slight erosion over 29.5 hr. period with cell voltage increasing from 5.8 to 22 V. Current efficiency was about 18% as calculated from loss of sodium chlorate. After this, sample was soaked in 50% HF for 16 hrs., rinsed in H_2O and retested in cell. Cell voltage increased from 6.2 to 25.2 V. in 3 hours.
Calcined tempered Masonite impregnated with silicon	3-25	20,050	4.5	100	5.0-7.6	12	Anode operated 29.5 hrs. converting 84% of sodium chlorate as shown by analysis for sodium chlorate and at a current efficiency of 53% based on $NaClO_4$ formed. Some erosion which finally caused formation of hole in sample after 42 hrs. of electrolysis. Operated at comparatively low voltage with no explosions.
Calcined Compreg, impregnated with silicon	3-26	25,500	5.6	100	5.6-12.0	12	Operated 17.5 hrs. with some erosion. Cell voltage did increase appreciably.

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(Continued)

Table XXV, (cont.) (5)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Effect on Anode
Calcined lofting board impregnated with silicon.	3-27	60,600	1.5	200	4.6-22	27	Erosion with holes appearing in anode sample after about 50.5 hrs. of operation. Current efficiency ranged from 56 to 34% for short periods (22.5 amp.-hrs.) but became much lower for long periods.
Calcined black tempered Masonite impregnated with silicon.	3-28	39,200	1.5	115	4.0-4.5	27	Some erosion with no explosions. Current efficiency was about 75% for a short period of electrolysis (22.5 amp.-hrs.) but was much lower for longer periods.
Calcined Duolux tempered Masonite impregnated with silicon.	3-29	38,600	1.5	200	5.0-8.4	27	Erosion with anode sample eroding in half at electrolyte level after 12 hrs. of operation.
Calcined Panelwood Masonite impregnated with silicon.	3-30	76,500	1.5	115	4.2-18	27	Some erosion without explosions. Operated at current efficiency of about 43% for a short period (22.5 amp.-hrs.) but dropped off appreciably with longer periods of electrolysis.
Calcined Preswood Masonite standard impregnated with silicon.	3-31	49,100	1.5	115	4.8-16	27	Some erosion but no explosions. Current efficiency was about 55% for a short period (22.5 amp.-hrs.) but fell off with longer periods of electrolysis.
Dense Cotton Batting, calcined and impregnated with silicon.	3-32	-	2.7	200	6.0-20.0	20-26	Some erosion with cell operating at about 50% current efficiency for a period of 30 amp.-hrs. With longer periods current efficiency dropped to about 20%.

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TABLE XXVI
HEATING AND QUENCHING TREATMENTS
CATEGORY NO. 4

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm. x10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Durhy - made by siliconizing a carbon rod formed by extruding; annealed at 1350°C. for 8 hours	4-1	- -	1.6-5	200	6-9	15-21	Anode shattered at top surface of electrolyte after explosions at cell.
			4.8-5	200	7-10	2-8	Anode shattered into two large pieces.
Durhy - same as sample No. 4-1 except annealed at 1350°C for 16 hours.	4-2	- -	3.3-5	200	6-9	17-20	Anode shattered into 3 large pieces.
			0.5-5	200	6-10	2-8	Anode shattered into 2 large pieces.
Durhy - same as sample No. 4-1 except annealed at 1350°C for 24 hours.	4-3	- -	3-5	200	5-9	14-17	Anode shattered into 3 large pieces.
			2.5-5	200	6-8	2-5	Anode shattered into 3 large pieces.
Durhy #2 (extruded) cooled from 1350°C to room temp. at 80° per hour	4-4	- -	4	200	10-18	20	Some explosions with spalling of anode surface within one hour.
Durhy #2 (extruded) quenched in H_2O from 1350°C.	4-5	- -	4	200	9-11	20	Several explosions within 1/2 hour resulting in shattering anode into several pieces.
Durhy #2 (extruded) quenched in molten lead from 1350°C.	4-6	- -	4	200	6	20	Very slight erosion - electrolyte turned brown gray. No spalling observed. Small amount of ppt. in electrolyte after 5 hrs. of electrolysis.
Extruded Durhy #2, quenched in molten lead from 1350°C.	4-6	17,800	2.6,3.0, 3.24	177,200, 205	..8-14.0	12	After 14.5 hrs. electrolysis with cell voltage increasing from 4.8-7.0v and with some erosion of the lead from the sample as evidenced by the muddy color of the electrolyte, one large piece of anode was blown off. Sample was then soaked in 35% HNO_3 for 3 days and after 15 min. of operation in cell, there was a small explosion. Then soaked in H_2O for 24 hrs. and tried in cell again with frequent explosions, finally causing anode to break in half at electrolyte level. (See sample No. 4-11)

(CONTINUED)

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TABLE XXVI, (cont.) (2)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp. °C.	Effect on Anode
Durhy #2, heated at 1600°C in an Induction Furnace for 2 hours.	4-7	- -	4.5	200	5.5-20	17-32	Surface spalling with explosions begins after 2-1/2 hrs. electrolysis. Voltage rises to 14v in same period.
Durhy #2, extruded stock, heated at 1600°C. for 5 hrs. in an oil fired kiln.	4-8	21,800	2.0	100	4.8-7.2	11-44	Exploding anode with chunks of anode being eroded off. After 3 hrs. anode blew apart a little below electrolyte surface with 1 large explosion breaking beaker containing electrolyte.
Durhy #2, extruded stock, fast (high temp) impregnation	4-9	3,460	2.0	100	4.6-12.0	11-14	Erosion, turning water-white electrolyte gray. After 2.5 hrs. anode blew apart above electrolyte surface with one large explosions.
Durhy #2, extruded stock, slow (low temp) impregnation	4-10	6,080	2.0	100	4.6-7.0	14	Frequent explosions with loose anode material being suspended in electrolyte. After 6 hrs. anode blew apart and broke beaker.
Cast Durhy #2, quenched in molten lead from 1350°C.	4-11	128,000	3.24	213	5.8-15.0	12	Exploding anode with small chunks of anode material falling off. Increase in cell voltage from 5.8-15.0 v in about 1 hr. Explosions finally blew sample in half after about 1 hr. of operation. Second sample behaved similarly.
Extruded Durhy #2, quenched in molten sodium nitrate from 1350°C.	4-12	41,800	3.24	184	12.0	12	Exploding anode. Anode blew off slightly below electrolyte level after 10 min operation. Second stage behaved similarly.

TABLE XXVII

SURFACE TREATMENTS, CHEMICAL AND PHYSICAL, AND ATMOSPHERES

CATEGORY NO. 5

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Description of Anode Material	Sample No.	Specific Resistivity ohm-cm $x10^{-6}$	Average Cell Current (amperes) *	Anode Current Density (approx.) ma/sq.cm.	Avarage Cell Voltage	Cell Temp °C.	Effect on Anode
Durhy - made by siliconizing a carbon body formed by casting; surface smoothed by grinding on a diamond wheel	5-1		0.3-9.0	200	10-20	3-7	Polarized; slight spalling.
			0.2-9.0	200	6-14	14-16	Polarized; slight spalling.
Durhy #2 put through a decarbonizing treatment - 50% reduction in free carbon	5-2		0.5-1.3	200	13.4-28	26	Polarized.
			1.0-2.8	200	10.0-27.6	26-28	Polarized.
Durhy #2 (extruded) tumbled in SiC grain for 50 hours	5-3		4	200	6-10	19-26	Severe spalling with numerous explosions in cell.
Durhy #2 (extruded tumbled in Al_2O_3 grain for 50 hours	5-4		4	200	5-11	20	Severe spalling within one hour resulting in shattering anode into several pieces.
Durhy #2, treated in HF + HNO_3 + H_2O solution	5-5		4.5	200	5.1-9.2	20	Rapid surface erosion and spalling; no explosions noted.
Durhy #2, treated in HF + H_2O solution.	5-6		4.5	200	5.1-7.6	17	Severe spalling of surface with numerous explosions after 2 hrs electrolysis. There was also a moderate normal surface erosion.
Durhy #2, treated in NaOH solution.	5-7		4.5	200	5.2-8.4	20	Rapid surface erosion and spalling; no explosions noted.
"Globar" heating section treated in H_2O and HNO_3	5-8	136,000	2.64	200	6.6-36	12	Increase in cell voltage from 6.6 - 36 v after 1 hr. operation. Appreciable erosion particularly at electrolyte level with sample finally breaking off at this point.
"Globar" heating section treated in HF and H_2O	5-9	124.000	2.64	200	6.0-34	12	Appreciable erosion particularly at electrolyte level with sample finally breaking off at this point. Increase in cell voltage from 6.0-34v after 1 hour operation.

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TABLE XXVIII
IMPREGNANTS (OTHER THAN SILICON) AND COATINGS
CATEGORY NO. 6

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Globar Heating Element Furfural impregnated, treated with HCl, then calcined at 900°C.	6-1	- -	0.5	25	28	17	Anode resistance is too high. A powdery substance separates from anode and floats on electrolyte surface.
Globar heating element, coated with Pt. by heating in H_2PtCl_6 solution	6-2	- -	4.5	200	10-24	15	Voltage rises rapidly after 1 hr electrolysis; slight erosion of surface; anode is hot at current contact.
Globar heating section impregnated with linseed oil	6-3	9,350	2.2	100	60	21-29	Shut off after 1/2 min operation because of high cell voltage required.
Durhy #2(extruded) impregnated with linseed oil.	6-4	4,320	2.3	100	6.3-9.0	12-14	After 2.25 hr. anode had a thick sticky covering, probably linseed oil. At 3.25 hrs exploding anode broke cell beaker. At 4.14 hrs exploding anode broke new cell beaker. Evidence of spalling on anode sample.
Globar heating section impregnated with silicone water repellant #DC 1107	6-5	37,400	2	100	70	17.5	Anode became very hot after 2 min. operation. Shut off because of high voltage required to operate cell.
Durny #2(extruded) impregnated with silicone water repellant #DC 1107	6-6	4,190	2.3	100	6.4-20	12-14	Exploding anode after 2.5 hrs quiet operation. After 7.75 hrs, evidence of severe spalling of anode. Cell voltage decreased after exploding anode blew chunks of material off.
Globar heating section impregnated with paraffin	6-7	18,700	2.2	100	30-34	21-47	Ran 12 min. Smoking anode lead contact. Shut off because of high cell voltage required.
Durhy #2(extruded) impregnated with paraffin	6-8	4,280	2.3	100	4.7-13.0	12-14	Exploding anode after 2.5 hrs quiet operation finally breaking cell beaker and cooling coil at 3.25 hrs. Anode also broke in half.

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TABLE XXIX
CAST SILICON
CATEGORY NO. 7

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x 10^{-3}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Cast silicon metal rod	7-1	- -	0.2-2	200	Greater than 20	3-5	Polarized almost immediately
Rod cast silicon metal, melted in helium atmosphere	7-2	2,600	2.64	147	26-70.0	12-30	No erosion. Increase in cell voltage from 26 to 70 after 1.5 hours of operation.
VARIATIONS IN PHYSICAL DIMENSIONS - CATEGORY NO. 8							
3 thicknesses of Masonite welded together by impregnating with silicon	8-2	17,850	1.8	113	4.4-19	12-15	After 6.3 hrs operation, individual layers of masonite began falling off and cell began exploding. After 9.8 hrs. operation sample had completely broken off at electrolyte level.
COATED GRAPHITE OR CARBON - CATEGORY NO. 9							
Graphite rods coated with silicon carbide crystals.	9-1	- -	2.9-3	200	6.8-9.4	24-25	Eroded through SiC coating; graphite severely eroded.
		- -	2.8-2.9	200	5.4-14	25.27	Severe erosion of graphite; electrolyte black.

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TABLE XXX
MISCELLANEOUS
CATEGORY NO. 10.

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm. x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Durhy #1 rodss; no free carbon in these rods.	10-1	- - -	0.2-1	200	20-22	6-9	All samples rapidly polarized in 10-15 min. No appreciable erosion.
Carbonized Masonite	10-2	47,200	2.5	200	9.5-14.0	- -	Eroded particularly at electrolyte surface, finally breaking apart at that place.
Cold pressed silicon carbide recrystallized in helium	10-3	2,200,000	3.7	178	20-30	12	No appreciable erosion. Heavy smoke from anode. Increase in cell voltage from 20v - 30v over 5 min period of electrolysis. No explosions observed during this time.
Non-porous graphite received from Pennsalt, heated in molten silicon	10-4	1,280	3.0	194	4.6-9.0	12	Very rapid erosion of sample. Electrolyte black with suspension of anode material after 34 min operation. Increase in cell voltage from 4.6v - 9.0 v over 3.5 hrs. electrolysis. Anode failed by complete erosion of all immersed area.
Refrax 10, Si_3N_4 bonded silicon carbide heated to 1900°C. to decompose the Si_3N_4.	10-5	255,000	2	95	5.0-15.0	12	Extremely heavy erosion, particularly at electrolyte level; bottom of sample dropped off after 1 hr operation. No explosions.
Refrax 20, Si_3N_4 bonded silicon carbide heated to 1900°C to decompose the Si_3N_4.	10-6	417,000	2	100	7.4-32.0	12	Extremely heavy erosion, particularly at electrolyte level; bottom portion dropped off after 1-1/3 hrs operation. No explosions.

(Continued)

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TABLE XXX, (continued) (2)

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Description of Anode Material	Sample No.	Specific Resistivity ohm-cm. x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/Sq.cm.	Average Cell Voltage	Cell Temp. °C.	Effect on Anode
Calcined extruded material "dry shot". In shooting this material, only sufficient silicon was placed in the crucible to theoretically convert the carbon in the piece to silicon carbide without leaving any excess silicon.	10-7	6,920	3.2	154	4.8-7.8	12	Noticeable erosion with finally a cell explosion breaking cell beaker and anode sample in half after 3.3 hours of operation.
Hot pressed Beta silicon carbide	10-9	62,100	1.0	100	4.6-7.8	20-40	Heavy erosion with no explosions. Sample has wick action on electrolyte.

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REFERENCES

(1) Final Report - Project NR 356-338, Contract NONR-1213(00); Providence College, Providence, Rhode Island, Dec. 31, 1953.

(2) Schumacher, J.C., Trans. Electrochem. Soc. 92, 45-53 (1947)

(3) Thomas, Upton, B., Trans. Electrochem. Soc. 94, 42-49 (1948)

(4) Palmer, W.H., Z. Electrochem. 29, 415-28 (1923)

(5) Pennsalt RNB 1400:126

(6) Letter, Rose, C.G./Gall, J.F., April 27, 1953 (Machining of Lead Dioxide)

(7) Kehoe, R.A., Thamann, F., and Cholak, J.J., Ind. Hyg., 15, 257,291 (1933)

(8) Kato, Yokogoro and Koisumi, Katsunaga, J. Electrochem. Assoc. (Japan) 2, 309-312 (1934) (same as Reference 18 of 1952 report)

(9) Kato, Y., Sugino, K., Koisumi, K. and Kitahara, Electrotech J. (Japan) 5, 45-48 (1941) (same as Reference 3 of 1953 report)

(10) Sugino, Michiro, Bull. Chem. Soc. Japan, 23, 115-120 (1950)

(11) Sugino, Michiro, Jap. Patent No. 173,460, August 16, 1946

(12) Pennsalt Report - Investigation of Methods to Produce Perchlorate Without the Use of Platinum - Part II - Project NR 352-263/2-19-15, Contract Number NONR 372(00) - Office of Naval Research

(13) Storey, O.W., Steinoff, E. and Hoff, E.R., Trans. Electrocham. Soc. 86, 337-343 (194)

(14) Letter, Rose, C.G./Gall, J.F., April 27, 1953 (Preparation of Samples)

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PERSONNEL ENGAGED IN EXPERIMENTAL WORK

J. F. Gall, Project Director
H. C. Miller, Group Leader
J. C. Grigger, Chemist
F. D. Loomis, Chemist
E. S. Hitelman, Laboratory Assistant
G. E. Webb, Laboratory Assistant
W. J. Barry, Laboratory Assistant

EXPERIMENTAL WORK RECORDED IN RESEARCH NOTEBOOKS

1951	1217:	1-196
1952	1217:	196-200
	1258:	1-200
	1289:	1-200
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	1365:	1-75
	1367:	1-73
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1954	1367:	73-200
	1400:	1-200
	1431:	1-200
	1433:	1-58
	1449:	1-136
	1467:	1-96

Henry C. Miller

John C. Grigger

Frederick D. Loomis

APPROVED:

J. F. Gall

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